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THE CHEMISTRY

OF

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THE CHEMISTRY

OF

PHOTOGRAPHY.

NATURE SERIES

THE CHEMISTRY OF PHOTOGRAPHY

BY

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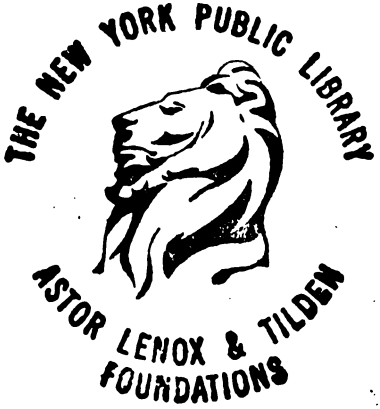

PREFACE.

THE lectures forming the subject of this little volume were delivered during the spring term of last year as a special course at the Finsbury Technical College, and were addressed to a mixed audience, composed of chemical students and practical photographers. In selecting the present topic, there has been no attempt to impart instruction in the manipulative details of Photography, since there are already before the public a large number of excellent works dealing with this branch of the art. It is only with the chemical principles underlying the subject that these lectures attempt to deal, and it is hoped that the mode of treatment adopted may serve the purpose of convincing photographers how essential is some

knowledge of Chemistry for the successful carrying on of their operations. With respect to students of technical science, it is always a most useful intellectual discipline to have presented in a systematic form the application of the general scientific principles which form the subjects of their every-day studies to some particular branch of technology. The interest evinced in the lectures, both by students and practitioners, has encouraged me to offer them in the present form, which is substantially the same as that adopted for delivery. In the lecture theatre, it is of course, impossible to give authorities for all the statements made, and such a series of references would have hampered the text to an extent quite out of proportion with the scope of the work. It will be seen, however, that I have endeavoured, as far as possible, to do justice to all those investigators to whom the subject is indebted for leading discoveries. Free use has been made of the writings of the late Robert Hunt, of Dr. J. M. Eder, Capt.

Abney, and Hauptmann Pizzighelli. I gladly acknowledge the assistance which I have derived from the published works of these well-known authorities.

The claim of Photography to be recognized as a branch of Chemical Technology is now generally admitted, and systematic courses of instruction in this subject are given in many institutions throughout the country. The operator who treats his art as though it consisted simply of a miscellaneous collection of recipes is bound to become superseded in this, as in all other departments of scientific industry, unless he has sufficient training in general principles to enable him to meet new and ever-changing conditions. It is to be regretted that purely scientific chemists have of late years shown a tendency to neglect the Chemistry of Photography as being an uninviting branch of their science. I venture to hope that the present work may contribute towards convincing such workers that there are many important problems still

awaiting solution in this field of research. Its high scientific interest is forcibly expressed by a saying of the late Col. Russell's, that Photography would be a most interesting subject *were it not for the pictures.*

In order to facilitate the teaching of the scientific principles of Photography, a number of experiments have been introduced, hints for the performance of which are given in the appendix to each lecture, the bracketed capitals in the text referring to these demonstrations. It is believed that the directions will be found sufficiently explicit to enable any lecture demonstrator possessed of ordinary skill in photographic manipulation to repeat them successfully. A large number of these experiments are believed to be new as lecture demonstrations, and the instructions have in these cases been given in somewhat greater detail. All the experiments described have been repeatedly performed, and they have been devised with the object of illus-

trating the various points which they are intended to elucidate with the simplest appliances and in the readiest possible way. All experiments of great delicacy requiring much previous preparation have for this reason been excluded. An electric arc light and lantern are indispensable for many of the demonstrations, but these are now such very general accessories in all properly-equipped lecture-rooms that their existence has been taken for granted.

I have great pleasure in acknowledging the skilful assistance which I have received in carrying out the experiments from Mr. T. H. Norris, Lecture Demonstrator, and from Mr. J. M. Smith, one of the Students of the Chemical Department, who kindly volunteered his services in helping to illustrate the lectures.

FINSBURY TECHNICAL COLLEGE,
February, 1889.

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THE CHEMISTRY

OF

PHOTOGRAPHY.

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LECTURE I.

Definition of Subject.—Photo-physical and Photo-chemical Change—Photo-chemistry of Iron Salts; of Copper, Mercury, Uranium, Gold, and Platinum Salts.—Photo-reduction of Chromates.—Dissociation and Oxidation.

THE subject of Photography, which has been chosen for this session's course of special lectures, appeals to us both as an art and as a science. The applications of photography to the production of pictures, either landscapes or portraits, and its uses in the service of the engraver or lithographer may be regarded as so many branches of technical art. With this aspect of the subject it is not proposed to deal on the

present occasion. It is more with the scientific principles underlying photography that I wish to engage your attention during this course, because in the first place these principles concern our Chemical Department as constituting a branch of technical chemistry, and because in the next place I am disposed to believe that the art is in danger of outstripping the science. This is a state of affairs which we often witness when a discovery of immediate practical utility is made. There are many branches of industry which are now suffering in this country because they have been allowed to go on from the time of their foundation without any attention being paid to the scientific principles underlying them. It has been found by a long course of experience that certain results can be obtained in a particular way and that mode of procedure has become stereotyped into a kind of article of faith. In such cases no trouble is taken to ascertain *why* the particular mode of operation leads to the desired results—the art has here outstripped the science.

But if we thus allow a useful discovery to degenerate into a purely empirical industry, we are neglecting our duty to that science which first gave us the discovery; and not only this, but we are running into the danger of seeing the industry taken out of our hands by more scientific competitors who have no stereotyped formula and who have taken the trouble to investigate the why and wherefore of the different steps in their processes. I do not for a moment wish you to understand that photography is particularly an English discovery, but there can be no doubt that this subject has suffered considerably in its scientific development by the haphazard experimenting of its unscientific devotees. Neither must it be forgotten that some of the greatest advances in the subject have been made by our own countrymen. When therefore I allude to that state of affairs in which there is a chance of e art going beyond the science as being a ndition fraught with danger, I simply wish imbue you with that spirit of investigation

which is the life and soul of advancement in every department of knowledge, in order that we in this country may not fall short in our contributions to the future development of the subject.

On considering the mode of treatment to be adopted in the present course the usual difficulty of selection presented itself. It is obvious that in such a wide field as that offered by photography but little information of value can be given in a short series of lectures unless the treatment is restricted to somewhat narrow limits. For not only has the subject its purely artistic side, which may be at once dismissed as beyond our present scope, but even in its scientific aspects it offers inviting paths opening in many directions. Thus the apparatus used by photographers, the theory and construction of lenses for the various kinds of work, the proper arrangement and illumination of subject and object, etc., might very well form the subjects of a course of lectures on the optics of photography—a

branch into which it is not proposed to enter on this occasion. Then again the chemistry of photography is capable of being dealt with in several ways, between which we have to make a choice.

The photographer in the course of his practice has necessarily to make use of various chemicals which he generally procures ready prepared and of a purity guaranteed sufficient for his purpose. In these days, when photography has been so simplified by the introduction of dry plates that the camera is becoming quite a common addition to the baggage of the tourist, the requirements of the amateur can be met at every stage, and the practical manipulative details are thus reduced to the extreme of simplicity. Both professionals and amateurs would however derive benefit from a knowledge of the chemistry of the materials which they so constantly employ—that is to say from a knowledge of the methods of preparation, the characteristic properties and reactions, and the modes of valuation of these materials. In other words, we may have a branch of the science dealing

with the chemistry of photographic materials—a kind of *materia photographica.* But inasmuch as this sort of information, although of undoubted value, is not absolutely essential to successful work in photography, and since those who require it can find it in many of the published manuals, I think I can more profitably occupy both my own time and yours by dealing with the subject from a somewhat higher point of view.

The future advancement of photography, as of all other branches of science, depends upon a proper recognition and application of scientific principles. It will be my endeavour therefore to make clear to you in the course of these lectures our present position with respect to the chemistry of photographic processes, so that you may see on the one hand what principles are involved in these processes, and on the other hand that you may realize how much we have yet to learn and in what directions further advance seems necessary. From this declaration of plan it will be seen that it is no part of my scheme to offer instruction in practical photography; the details of processes

will only be given in so far as necessary to enable you to understand the principles underlying them. I have decided upon this mode of treatment—I may add after much consideration—because, as it seems to me, our knowledge of the chemistry of photographic reactions is still involved in much obscurity, and a wide field of investigation has yet to be explored before the subject can be established on a truly scientific basis.

The action of light with which we are chiefly concerned in photography is a photo-chemical action resulting in the decomposition of certain compounds—usually salts of silver—and the subsequent completion of the reaction by the application of appropriate chemicals. By a photo-chemical action must be understood a chemical change produced by the action of light. It is essential to bear in mind that we are mainly concerned with actions of this kind because the influence of light does not always induce changes of a purely chemical nature. We may have *physical* changes in matter produced by light, and it is sometimes difficult to decide in any particular

case how much of the effect is due to physical and how much to chemical change. That light may induce purely physical change will be evident on reference to the numerous recorded instances, a few of which may be here mentioned.

It is well known that under the influence of light such elements as sulphur and phosphorus gradually become transformed into their so-called "allotropic" modifications, ordinary phosphorus becoming red or amorphous and a strong solution of sulphur in carbon disulphide slowly depositing the insoluble modification when exposed to sunlight in a sealed tube [A]. So also certain metallic salts, such as the crystalline chloride or iodide of silver, nickel sulphate and zinc selenate, experience a change in crystalline form under the influence of light.

These are a few examples of photo-physical changes requiring more or less time for their completion. In some instances light is known to produce an instantaneous change. Crystalline selenium, which under ordinary circumstances is a very bad conductor of electricity, becomes a

much better conductor when light falls upon it, the conductivity again falling off in the dark; this property of selenium, discovered by Willoughby Smith in 1873, has been utilised in Bell's photophone. All these instances are illustrations of physical changes induced by light—the chemical composition of the substances referred to is in no way altered: white and red phosphorus are chemically identical, so are the soluble and insoluble modifications of sulphur, and the same is true of the different crystalline forms assumed by a salt such as nickel sulphate or zinc selenate.

Regarded as a chemical agent light may produce both combination and decomposition, although it is often very difficult to say whether any particular effect is the result of one or the other or of both modes of action. Consider for instance one of the most familiar cases, the action of light upon a mixture of chlorine and hydrogen. These gases, as is well known, react explosively under the influence of a strong light to form hydrogen chloride [B]. This is usually spoken of as a case of combination, but it is highly probable

that a decomposition of the molecule of chlorine precedes its union with the hydrogen. The reason for believing in such preliminary decomposition is that the rays which are most active in bringing about the reaction are the blue and violet, *i.e.* just those rays which are absorbed by chlorine.[1] Without attempting therefore to draw any hard and fast line between decomposition and combination, let us pass on to the consideration of some of the photo-chemical reactions which are likely to be of interest, either directly or indirectly, in connection with our present subject. It is advisable to approach photography from this broad point of view because we have now become so accustomed to associate photographic processes with the salts of silver that there is a danger of forgetting the fact that other compounds are also possessed of photo-susceptibility.

As examples of reactions promoted or caused by light let us first consider some of the more

[1] According to some researches recently published by Pringsheim (*Ann. Phys. Chem.* Ser. 2, vol. xxxii. p. 384), water vapour is essential to the reaction.

familiar cases which may be said almost to obtrude themselves under the notice of chemists who are in the habit of keeping reagents on shelves exposed to light. It is well known that chlorine water under the influence of light gradually becomes acid from the formation of hydrochloric acid, whilst oxygen is liberated. It is instructive to compare this change with the same reaction brought about by heat. By passing steam and chlorine through a red hot tube hydrogen chloride and oxygen are formed [C] according to the equation :—

$$2Cl_2+2H_2O=4HCl+O_2.$$

An aqueous solution of hydriodic acid also is gradually decomposed by light and becomes brown from the liberation of iodine. This reaction is of interest from our present point of view because it is not a simple case of the resolution or dissociation of a compound into its constituents, but a reaction in which the oxygen of the air takes a part :—

$$4HI+O_2=2H_2O+2I_2.$$

The proof of this is that the change does not occur when air is excluded. In the presence of air an aqueous solution of hydrogen iodide undergoes the same decomposition in the dark, only more slowly, so that in this case light acts as an accelerator of a chemical change which takes place less rapidly in the dark.

The action of light upon metallic compounds such as the oxides and salts is, speaking in general terms, a reducing action, so that it is important to remember that the metallic compounds which show the most striking photo-chemical changes are very generally those which are capable of being reduced from a higher to a lower state of oxidation. Among the metallic compounds which chemical students are in the habit of regarding as typical of those capable of forming two such classes, the salts of iron will at once suggest themselves. It is well known that ferric salts in the presence of reducing agents lose some of their oxygen or other negative constituent and become converted into ferrous compounds. This reduction can also be effected by light. It must be

understood however that the photo-chemical change can only take place in the presence of oxidizable matter, so that the reduction of the ferric salt and the oxidation of the associated substance proceed simultaneously.

The photo-sensitiveness of ferric compounds has long been known, having been first systematically examined by Sir John Herschel, to whom photography was in its early days indebted for many important contributions. As a type of photo-chemical change it will be instructive to enter somewhat further into these reactions on the present occasion. Let us start from purely chemical considerations:—

Reducing agents such as nascent hydrogen, sulphurous acid, &c., immediately reduce ferric compounds [D] either in the presence or absence of light:—

$$\underset{\text{Ferric sulphate.}}{Fe_2(SO_4)_3} + SO_2 + 2H_2O = 2FeSO_4 + \underset{\text{Ferrous sulphate.}}{2H_2SO_4}$$

Here the reducing agent, sulphur dioxide, becomes oxidized into sulphuric acid at the ex-

pense of the oxygen of the ferric salt. Now when light falls upon an aqueous solution of a ferric salt—say ferric chloride—no reduction takes place, because under these circumstances the solvent water does not act as a reducing agent; but in the presence of organic compounds which are easily oxidized, and which therefore absorb oxygen or other negative elements, or, in other words, which act as reducing agents, ferrous chloride is formed. Thus an ethereal or alcoholic solution of ferric chloride is reduced by light [E]. In the case of alcohol the change might be represented thus :—

$$\underset{\text{Ferric chloride.}}{Fe_2Cl_6} + \underset{\text{Alcohol.}}{C_2H_6O} = \underset{\text{Ferrous chloride.}}{Fe_2Cl_4} + \underset{\text{Aldehyde.}}{C_2H_4O} + 2HCl.$$

If therefore we have a ferric salt in contact with something that will act as a reducing agent, we can insure the formation of a ferrous salt on exposure to light. You must notice the expression *will act*, because the whole secret of the photo-chemical action is involved therein. We do not want a substance that *does act*, such as sulphurous acid,

but a compound ready to act when, under the stimulus of light, the substance with which it is associated is decomposed: we must have a system ready to undergo rearrangement, but waiting the application of some external energy to set it off.

In order to utilize the photo-reducibility of a ferric salt for the production of a picture we may spread the salt over a surface of paper because this, being an organic substance, acts as the reducing agent. Of course it comes to the same thing if we use an organic ferric salt. By exposing such a sheet of ferric-coated paper to the electric light for a short time under a design cut out in black paper, the portion exposed to the influence of light, *i.e.* the design, becomes delineated in ferrous salt, and thus becomes faintly visible, because of the lighter colour of the latter as compared with the yellow ferric compound. The contrast can of course be made more striking by washing over the exposed paper with a solution of some substance which forms a coloured compound with one salt and not with the other. Thus all chemists know that potassium ferricyanide gives

only a dark colouration and no precipitate with ferric salts, whilst with ferrous salts it forms a blue precipitate of ferrous ferricyanide (Turnbull's blue):—

$$3Fe_2Cl_4 + 2K_6Fe_2Cy_{12} = 2Fe_3(Fc_2Cy_{12}) + 12KCl.$$

By washing the exposed surface with a solution of ferricyanide the pattern therefore becomes revealed or, as photographers would say, *developed* in Turnbull's blue [F].

The photo-reduction of the ferric salt is sometimes accompanied by the visible evolution of a product of oxidation. This is the case with a solution of ferric oxalate which under the influence of light gives off carbon dioxide and deposits ferrous oxalate:—

$$Fe_2(C_2O_4)_3 = Fe_2(C_2O_4)_2 + 2CO_2.$$

The organic acid of the ferric salt here plays the part of the reducing agent, the reaction being sufficiently definite to enable it to be employed as a method of chemical photometry.

This behaviour of the iron salts under the in-

fluence of light will serve as a useful introduction to the photo-chemistry of other metallic salts. We may look upon these reactions as typical cases of the photo-reduction of a salt from a higher to a lower state of oxidation in the presence of organic reducing agents. The development by means of ferricyanide may from our present point of view be put into the background as being only of secondary importance. The one great lesson conveyed by the illustrations chosen is that the reducing action of light does not necessarily always mean a removal of oxygen, but other negative elements may also be removed and fixed by the reducing agent, such, for example, as chlorine when ferric chloride oxidizes alcohol or ether under the influence of light.

Without in any way attempting a complete treatment of the photo-chemistry of all the metallic salts which are influenced by light, it will be of interest to consider here some of the better known instances.

In the case of copper it is known that cupric compounds reduced to cuprous compounds, such for

example as an alcoholic or ethereal solution of cupric chloride, which becomes reduced to cuprous chloride under the influence of light. The action is here analogous to the photo-reduction of ferric salts and requires no special explanation. With respect to the reduction of cuprous chloride I shall have to say more hereafter.

Mercuric chloride in aqueous solution is slowly decomposed by bright light in the following manner:—

$$4HgCl_2 + 2H_2O = 2Hg_2Cl_2 + 4HCl + O_2.$$

Mercuric chloride. Mercurous chloride.

As oxygen is here liberated you will readily understand that in accordance with the principles previously laid down the reaction would be promoted by the presence of some oxygen-absorbing, *i.e.* oxidizable substance. It has accordingly been found that the addition of organic substances, such as formic, oxalic, succinic, tartaric, and other acids, sugar, &c. hastens the decomposition. Thus a mixture of mercuric chloride and ammonium oxalate under the influence of light gives off

carbon dioxide and rapidly deposits mercurous chloride [G]:—

$$2HgCl_2 + (NH_4)_2C_2O_4 = Hg_2Cl_2 + 2NH_4Cl + 2CO_2.$$

This decomposition, like the corresponding change undergone by ferric oxalate, proceeds at a measurable rate and has been utilized for the quantitative determination of the intensity of light.

Other mercuric salts, such as the nitrate, sulphate, carbonate, chromate, &c., when spread over the surface of a sheet of paper and exposed to light, also undergo reduction accompanied by a change of colour [H].

Uranic salts in contact with organic substances, such as alcohol, ether, glycerol, paper, &c., behave like the ferric compounds and undergo reduction on exposure to light. Uranous compounds no doubt result from this reduction, but the reactions have not been sufficiently studied from their chemical side to enable us to represent the changes satisfactorily by equations. It must be borne in mind that the so-called uranic salts are really salts of the oxygenated radical UO_2, uranyl,

so that in the photo-reduction this radical may part with its oxygen. Thus, in the case of uranyl sulphate dissolved in alcohol and exposed to light, uranous sulphate is deposited :—

$$2UO_2SO_4 = U(SO_4)_2 + UO_2 + O_2(\text{absorbed}).$$

The oxygen is of course not liberated, but is used up in oxidizing the alcohol, probably with the formation of acetic acid.

It must suffice for the present to mention that the sensitiveness of the uranic salts is sufficient to enable these compounds to be used for photographic purposes [I].

Good illustrations of photo-chemical reduction are furnished by the salts of gold. Thus a solution of auric chloride, $AuCl_3$, in contact with organic substances is reduced first to aurous chloride, AuCl, and then to metallic gold. The photographic importance of the easy reducibility of gold salts will be seen subsequently when we come to consider the chemistry of the process of toning.

The photo-reduction of the platinum salts takes place readily in the presence of organic substances,

especially when the platinous salts are used. The reduction, as in the case of gold compounds, proceeds to the extreme, metallic platinum being deposited in an extremely fine state of division. The two classes of platinum salts are typified by platinic chloride, $PtCl_4$, and platinous chloride, $PtCl_2$, both of which form double salts with the chlorides of the alkali metals :—

$PtCl_4,2KCl = K_2PtCl_6$. $PtCl_2, 2KCl = K_2PtCl_4$.
Potassium chloroplatinate. Potassium chloroplatinite.

The chromates are among those salts, well known to chemists as powerful oxidizers, which are easily reducible by light in the presence of organic or other oxidizable substances and which are of great importance in photography. The general character of the change which takes place when a chromate is reduced may be exemplified by the well-known reduction of potassium dichromate by means of sulphuric acid and alcohol :—

$K_2Cr_2O_7 + 4H_2SO_4 + 3C_2H_6O =$
Potassium dichromate. Alcohol.

$Cr_2(SO_4)_3 + K_2SO_4 + 3C_2H_4O + 7H_2O.$
Chromium sulphate. Aldehyde.

It is to be observed in this reaction that the dichromate, which is a salt of the acid chromic oxide, CrO_3, becomes reduced to a salt of the basic oxide Cr_2O_3 [J].

This reaction will serve to illustrate the general nature of the photo-reduction. A solution of potassium or ammonium dichromate spread over paper and exposed to light becomes brown on the exposed portions [K]. The paper (or its contained size) here plays the part of the reducing agent, just in the same manner that it does in the case of ferric chloride. Other organic substances, such as sugar, glycerol, albumen, gums, gelatine, &c., exert a similar influence. No free acid is necessary in these cases of photo-reduction; it appears indeed probable that the oxygen of the dichromate is used up in forming acid products of oxidation from the organic substances, so that the alkali would be thus neutralized. In the case of gelatine for example it has been proved that formic acid is among the products of its photo-oxidation by dichromate.

The dichromates moreover are themselves acid

salts, containing an excess of acid oxide, and it has been shown that the first step in their photo-reduction in the presence of an organic substance is in many instances, if not generally, the chromium chromate, Cr_2O_3, CrO_3 or Cr_3O_6, which compound is capable of further reduction :—

$$4Cr_3O_6 = 6Cr_2O_3 + 3O_2.$$

The action of light upon chromatized gelatine is the foundation of several important printing processes. By this action not only is the dichromate reduced, but the gelatine is at the same time rendered insoluble. It seems probable that the insoluble compound thus formed contains oxide of chromium as an essential constituent. It will be of interest here to remark that in this case we have another reaction in which light acts as an accelerator of chemical change, since chromatized gelatine becomes gradually insoluble *in the dark*, especially in a moist atmosphere.

We have now considered a sufficient number of nstances to enable us to realize more clearly the

general nature of the change which takes place when light acts upon reducible salts in the presence of oxidizable substances. It will in future be well to bear in mind that photo-reduction may mean either a liberation of oxygen or of some other negative element, such as chlorine—that is to say we must expand our ideas of photo-reduction so as to include dehalogenization as well as deoxidation. Although in the cases given an oxygen or chlorine-absorbing substance, *i.e.* a reducing agent, is essential to the reaction, it must not be supposed that all photo-chemical changes are of this character. It will serve to broaden our views if we now consider a few other typical illustrations.

In some instances light, like heat, can produce changes of the nature of pure dissociation, such for example as when mercurous oxide becomes converted into mercuric oxide and mercury, or mercurous chloride into the mercuric salt and the metal [L]:—

$$Hg_2O = HgO + Hg$$
$$Hg_2Cl_2 = HgCl_2 + Hg$$

So also certain metallic oxides, such as those

of gold and silver, give off oxygen and leave a residue containing the metal on exposure to light. All such decompositions as these may be regarded as cases of photo-dissociation.[1]

Under the influence of light the rate of oxidation by atmospheric oxygen is often accelerated, and it is probable that this photo-oxidation plays an important part in many photographic phenomena which we shall have to deal with hereafter. I may remind you of one illustration of this kind of action given in the early part of this lecture, viz., the oxidation of an aqueous solution of hydriodic acid with the liberation of iodine (see p. 11). In a similar manner potassium iodide, although stable when dry, gradually becomes alkaline and discoloured when exposed to light in a moist state, the change being due to photo-chemical oxidation by atmospheric oxygen [2]:—

$$4KI + 2H_2O + O_2 = 4KOH + 2I_2.$$

[1] Gaseous hydrogen iodide is decomposed by light; after exposure for a summer month to daylight 80 per cent. of the gas was found to be decomposed. G. Lemoine, *Ann. Chim. Phys.* ser. 5, vol. xii. p. 145.

[2] Vidan, *Pharm. Journ. Trans.* 3rd ser. vol. v. p. 383.

In this case the potassium iodide itself may play the part of the reducing agent, since it is known that this salt combines with two atoms of iodine to form the unstable triiodide, KI_3.

Other examples of oxidation are furnished by lead compounds, moist litharge becoming gradually deeper coloured and a thin film of lead sulphide becoming bleached on exposure to light and air [M]. So far as the chemistry of these changes is concerned the reactions are simple enough :—

$$6PbO + O_2 = 2Pb_3O_4$$
$$Pb_3O_4 + O_2 = 3PbO_2$$

In the case of litharge the first product is red lead and the final product the brown peroxide. In the case of the sulphide the sulphate is formed :—

$$PbS + 2O_2 = PbSO_4$$

Certain resinous and bitumenous substances when exposed in thin films to the action of light and air become insoluble in hydrocarbons and other oils which dissolve them freely before

such exposure. The action is here probably due to photo-oxidation, since air is essential. This particular kind of photo-chemical oxidation is historically interesting as having been the method employed in the first successful attempt to fix a photographic image by Joseph Nicéphore Niepce about the year 1824. This inventor—who, with Daguerre, must be considered as the founder of photography—coated a metallic plate with bitumen and exposed for some hours in a camera provided with a lens. The image was afterwards developed by immersion in oil of lavender, which dissolved the portions of the film unacted upon by light and left a picture in insoluble bitumen. The discovery of this, the first truly photographic process, laid the foundation of a printing process which is still in use.

Among other instances of the photo-chemical oxidation of carbon compounds may be mentioned the well known bleaching action of light upon certain natural and artificial colouring matters. Here for instance are examples of designs formed by the action of light upon papers dyed with

eosin and methylene blue, the former being sensitive enough to show a perceptible amount of fading on exposure to sunlight for ten or fifteen minutes [N].

The typical cases of photo-chemical action which have now been considered may be regarded as illustrative of a special branch of our science which may be termed photo-chemistry, and of this photographic chemistry in the sense here dealt with must be looked upon as an offshoot. There are of course many other kinds of chemical action effected by light upon which I should have been tempted to dwell if they could in any way have been directly connected with photographic processes. Thus the decomposition of carbon dioxide by the green leaves of plants, the photo-decomposition of the vapours of organic compounds such as amyl nitrite, isopropyl iodide, etc., investigated by Tyndall, the polymerisation of liquids like vinyl bromide, and the remarkable influence of light in determining the precise part of the molecule of a hydrocarbon attacked by chlorine or bromine recently in-

vestigated by Schramm,[1] are all types of photo-chemical action which would lead us too far astray if followed up in the present course of lectures.

[1] *Ber. Deutsch. Chem. Gesell.* 1885, vol. xviii. pp. 350, 606, and 1,272; *Ibid.* 1886, vol. xix. p. 212.

APPENDIX TO LECTURE I.

A (p. 8).—Two sealed glass tubes were exhibited both containing a portion of the same saturated solution of sulphur in carbon disulphide. One tube had been exposed to light for a week or two and contained a deposit of crystalline sulphur incrusting the side of the glass, while the other, which had been kept in the dark, was perfectly clear.

B (p. 9).—For details concerning the experimental illustration of the explosion of hydrogen and chlorine under the influence of light see Roscoe and Schorlemmer's *Treatise on Chemistry*, vol. i. p. 125.

C (p. 11).—Chlorine is passed through a flask containing boiling water and the mixed gas and water vapour passed though a porcelain tube strongly heated in a gas combustion furnace. The escaping gas is received over dilute caustic soda

solution to absorb excess of chlorine, and shown to be oxygen by the usual tests.

D (p. 13).—A solution of ferric chloride is divided into two portions, to one of which sulphurous acid or an aqueous solution of a sulphite is added. The two beakers are placed side by side on white paper and a few drops of potassium ferricyanide solution allowed to fall into each, the beaker containing the reduced iron salt giving a blue precipitate and the unreduced solution a brown colouration.

E (p. 14).—A solution of ferric chloride in alcohol (methylated spirit answers the purpose) is divided into two portions in two large test tubes, one of which is placed on the table away from the influence of light and the other in a beaker of water (to keep it cool) and exposed for five or ten minutes to the electric beam from an arc lamp concentrated by means of a lens. After exposure the two tubes are placed side by side and ferricyanide added to each, when the solution in the exposed tube gives a deep blue precipitate and the other the usual brown colouration.

F (p. 16).—Paper is coated with a 10 per cent. solution of ammonio-ferric citrate by floating on the liquid for a few minutes and then allowing it to dry in a dark room. After exposure for about

ten minutes to the electric light under a design cut out in black paper, the sheet is withdrawn and developed by brushing a solution of potassium ferricyanide over the surface.

G (p. 19).—The mixture of mercuric chloride and ammonium oxalate used in Eder's "mercury-oxalate photometer" can be employed in this experiment. The solution is made as follows:—

No. 1—4 grams crystallized ammonium oxalate.
100 c.c. distilled water.
No. 2—5 grams mercuric chloride.
100 c.c. distilled water.

Before use two volumes of No. 1 are added to one volume of No. 2 and the clear solution placed in a flask in the electric beam. The separation of the shining white crystalline mercurous salt soon commences, and forms a very striking lecture demonstration.

H (p. 19).—Dark mercurous oxide prepared by precipitating mercurous nitrate with caustic potash is collected on a filter, washed with water, and allowed to dry in the air in the dark. A test tube is filled with the dry powder and exposed to light for some days, when the side towards the light becomes ochreous owing to the formation of mercuric oxide, the other side remaining dark.

This tube was exhibited and also old specimens of various mercurial preparations which had been kept for a long time in a cupboard with glass doors, the sides of the bottles towards the light showing in many cases discoloration. Signs of decomposition were particularly noticeable in the case of a specimen of calomel.

I (p. 20).—Paper is floated on a 15 per. cent solution of uranium nitrate in distilled water for about ten minutes and then allowed to dry in the dark. The paper is exposed under a design for about fifteen minutes to the electric light and then developed with ferricyanide, as in the case of the ammonio-ferric citrate paper. It saves time if the paper is given a preliminary exposure before the lecture.

J (p. 22).—A hot solution of potassium dichromate of a distinct orange colour is placed in a beam of electric light in a flask and alcohol dropped in till the colour changes to green (red by transmitted light). The oxidizing action of chromic oxide was also shown by the familiar experiment of dropping alcohol on to the solid crystals, when the heat produced causes the alcohol to take fire.

K (p. 22).—A design was exhibited produced by exposing a sheet of paper coated with potassium

dichromate under a pattern cut out in black paper. The exposed portions are brown.

L (p. 24).—The specimens referred to in exp. H illustrate these reactions.

M (p. 26).—A design can be printed on paper coated with lead sulphide by floating on a solution of the acetate and then exposing to sulphuretted hydrogen till a brown surface is produced and drying in the dark. After some days' exposure to bright light the exposed portions become lighter.

N (p. 28).—Papers were coloured by floating on a solution of eosin (·25 grm. per litre) and methylene blue (·25 grm. per litre) and then exposed under a design in the usual way. In the course of about a week the exposed portions have faded sufficiently to render the design conspicuous, and after three weeks the blue and red patterns appear on almost a white background. Many other coal tar colouring matters, such as the methyl violets, iodine green, etc., are equally susceptible of photo-oxidation.

LECTURE II.

Photo-chemistry of the Silver Compounds.—Historical.—The Chloride; loss of Chlorine on exposure to Light.—Composition of Darkened Product.—Analogy of Silver Haloids with Cuprous, Mercurous, and Thallous Haloids.—The Bromide and Iodide.—Carey Lea's Experiments on the Photo-salts.

AMONG the photo-reducible metallic salts those of silver occupy such an important place in all photographic processes that their consideration has been deferred in order that they might receive their due share of attention in the present lecture. Not only are these salts of great practical importance at the present time, but they are historically interesting as having been the compounds in which a change of colour on exposure to light was first observed and recorded. I regret much that the

scope of the present lectures will not admit of lengthy historical digressions, and it must suffice here to mention that the darkening of the skin when touched by silver nitrate was known to Albertus Magnus in the thirteenth century. The darkening of native silver chloride (horn silver) on removal from the mine was described by Fabricius in the sixteenth century, and in the seventeenth century Glauber and Robert Boyle speak of the discoloration of silver compounds, although none of these earlier writers appear to have suspected that the darkening was due to the action of light. The first distinct statement as to the darkening of a silver compound being the result of the influence of light was made by a German physician, J. H. Schulze, who in 1727 observed that when a solution of silver in nitric acid was poured on to chalk the precipitate darkened on the side exposed to light, and he clearly proved by experiment that this effect was produced by light and not by heat.[1]

All the salts of silver, both inorganic and organic,

[1] Eder's *Handbuch der Photographie*, 1884, Part I., p. 2.

are more or less decomposed by light, especially and sometimes only in the presence of oxidizable substances. Thus an aqueous solution of silver nitrate is not acted upon by light unless organic matter or some other form of reducing agent is present. But although the various silver salts offer for consideration many instructive cases of photo-chemical action, it will be better to limit our attention to those which are of paramount practical importance in photography, viz.: the chloride, bromide, and iodide, known to chemists under the general designation of the silver haloids.

The fact that silver chloride becomes violet and finally brownish violet on exposure to light has been known since the middle of the eighteenth century, the earliest statement with respect to the precipitated chloride (as distinguished from native "horn silver") being attributed to Prof. Johann Baptist Beccarius of Turin. This property, so familiar to all students of chemistry, is, I need hardly remind you, utilized at the present time in our silver printing processes. The cases of photo-chemical decomposition which have been considered

in the last lecture will I am sure have prepared you for the first questions which we must now put to ourselves. What chemical change does the discoloration of silver chloride indicate? Is it a chemical change, or is it purely physical? Is it, if chemical, a process of dissociation, of double decomposition, or of oxidation? It will be interesting to us as chemists to consider how these questions have been answered.

It has been held by some authorities that the change is a physical one; that violet silver chloride has the same chemical composition as the unaltered compound. But this view may be dismissed at once, because it is certain that the chloride loses chlorine on exposure to light, a fact known to Scheele so far back as the year 1777. It has been shown by numerous analyses that the darkened chloride is poorer in chlorine than the white chloride. This may be regarded as a direct proof that the change is a chemical one, and there are moreover several methods by which the liberation of chlorine, or at any rate some chlorine containing gas, can be directly demonstrated [A]. Then we

have indirect proof that chlorine is given off in the fact that chlorine absorbents, such as silver nitrate, stannous chloride, or organic substances, accelerate the photo-chemical decomposition, thus reminding us of the action of alcohol upon ferric chloride under the influence of light. On the other hand oxidizing agents which tend to prevent the absorption of chlorine, such as mercuric or stannic chloride, ferric salts, or chlorine itself, retard the photo-decomposition, or, if present in sufficient quantity, prevent it altogether [B].

Taking it as established that the discoloration of silver chloride on exposure to light is a photo-chemical and not a photo-physical action, we have next to push our inquiries farther and to ask what chemical difference exists between the violet and white chloride. Beyond the fact that the violet chloride contains less chlorine it must be confessed that our chemical knowledge is still very deficient. It may be of service if I here point out exactly what we know and what we do not know with respect to this fundamental photo-chemical decomposition. You will find it generally stated in books

that the change is due to the formation of a subchloride of silver according to the equation :—

$$4AgCl = 2Ag_2Cl + Cl_2.$$

Now, whatever may be the plausibility of this reaction, it must not be forgotten that the existence of the subchloride is only inferred from the analogy of silver with the metals of the copper group, and is not the result of the analysis of the pure compound. Amongst the work published by the various chemists who have studied these compounds I can find no satisfactory proof that the subsalt, Ag_2Cl, has ever been isolated in such a form as to establish its chemical individuality. The notion that the subchloride is the product of the photo-decomposition of the normal chloride was first suggested in 1814 by Fischer, and was reiterated in 1834 by Wetzlar, and has since received general acceptance. It is not difficult to see why this suggestion has found its way into the books as though it expressed an established chemical truth. I have already said that it must be admitted that silver chloride loses chlorine

on exposure to light; hence it has been assumed that only one of two things could happen, viz. that the salt must be reduced to the metallic state, or to a sub-salt. On this assumption we should have in the first instance a mixture of metal with unaltered chloride, and in the second case a mixture of chloride and subchloride. Now it is well known that the darkening of silver chloride takes place under nitric acid, and it has also been found that this acid does not dissolve out any appreciable quantity of silver from the darkened chloride, so that it has been concluded that the latter does not contain any free metal. By that process of reasoning known as exclusion it has therefore been assumed that the other alternative holds good—that the darkening is due to the formation of subchloride.

What has modern chemistry to say with respect to the existence of the subchloride? From an *d priori* point of view we have, as already stated, the analogy suggested by the relationship of silver to copper and mercury, both of which metals form subchlorides. But we all know that

analogy, although at times a very useful guide, is apt to lead us into difficulties if trusted too implicitly. Let us turn in the first place therefore to a much safer principle, and see what laboratory work has done of late years towards the solution of the problem.

It must be confessed that the results in this direction have been somewhat unsettling as far as concerns the sub-salts of silver. One strong argument in favour of the existence of these salts has always been the supposed suboxide, Ag_4O, obtained in 1839 by Wöhler by reducing the citrate in a current of hydrogen at 100°C. But recent investigations by Muthmann,[1] by Friedheim,[2] and by Bailey and Fowler at Owens College[3] appear to me to render the existence of Wöhler's suboxide extremely doubtful, thereby making all the statements about the subchloride being formed by

[1] *Ber. Deut. Chem. Gesell.* 1887, p. 983.

[2] *Ibid.* 1887, p. 2554 and 1888, p. 307. See also papers by Pillitz (*Zeitschrift für Analyt. Chemie.* vol. xxi. pp. 27 and 496), by Spencer Newbury (*Amer. Chem. Journ.* vol. viii. p. 196) and by v. der Pfordten (*Ber. Deut. Chem. Gesell.* 1887, pp. 1458 and 3375; and 1888, p. 2288).

[3] *Journ. Chem, Soc. Trans.* 1887, p. 416.

the action of hydrochloric acid upon this suboxide equally doubtful.[1]

Such being the outcome of recent work upon the suboxide, we may now come back to the main question and ask whether the darkened chloride has ever been submitted to such an examination at the hands of chemists as to have furnished distinct evidence of the existence of the subchloride therein. In answer to this it must be admitted that the evidence thus far obtained goes no farther than to show that the darkened chloride contains less chlorine than the unaltered chloride. This result has in nearly all cases been arrived at by determining one constituent only, either the silver or the chlorine, and then representing the loss of chlorine as corresponding to the formation of so much subchloride. By this means different experimenters have given different estimates of the amount of subchloride formed. Carey Lea for example states that when

[1] The substance obtained by this means has according to v. Bibra the formula Ag_4Cl_3 (*Ber. Deut. Chem. Gesell.* 1875, p. 741), but the above quoted investigations tend to show that it is a mixture and not a definite chemical compound.

silver chloride is exposed under water for five days one per cent. is reduced to subchloride, and Riche asserts that after exposure for a year and a half the formula of the reduced salt corresponds to Ag_3Cl_2. But it will become evident on consideration that such methods can never give satisfactory evidence as to the formation of the subchloride, because the existence of this salt is first assumed and the loss of chlorine then attributed to its production—as clear a case of circular reasoning as one could wish to meet with.

So far then we get no justification for the belief in the formation of silver subchloride by the photo-reduction of the white chloride. The product, whatever it may be, is not definite enough to be identified as a sub-salt by its chemical characteristics with the same sharpness that we can distinguish between other chlorides and subchlorides, such, for example as mercuric and mercurous or cupric and cuprous chlorides. By the action of solvents which are known to dissolve silver chloride, such as sodium thiosulphate, potassium cyanide, or ammonia, the darkened chloride

always leaves a residue of metallic silver. But here again we get no real information as to the presence of a sub-salt, because the existence of the latter is assumed and the action of the solvents represented by such equations as these :—

$$Ag_2Cl + Na_2S_2O_3 = AgNaS_2O_3 + NaCl + Ag$$
$$Ag_2Cl + 2KCN = AgK(CN)_2 + KCl + Ag$$
$$2Ag_2Cl + 3NH_3 = [2AgCl + 3NH_3] + 2Ag.$$

But these equations seem, to say the least of them, somewhat improbable, because if the sub-chloride were such an unstable compound as to be decomposed by these solvents it is hardly likely that it could be formed in the presence of such a powerful oxidizer as nitric acid. Nevertheless it is well known that silver chloride darkens under nitric acid and, although somewhat less rapidly, even under the strongest acid.

Now let us consider the arguments from analogy and see what value really attaches to them. The nearest analogues of the silver haloids are the corresponding salts of mercury, copper, and thallium. Thus the insolubility of mercurous,

cuprous, and thallous chlorides reminds us of silver chloride, so that if analogy shows anything it must lead us to believe that silver is the analogue of copper, mercury, and thallium in the cuprous, mercurous, and thallous states. This is admitted by all chemists; but when it is asserted, as we sometimes find in books, that the existence of a silver subchloride is rendered probable by the existence of cuprous or mercurous chloride, the analogy has been over-strained. Silver is strictly speaking not analogous to copper and mercury, but to cuprosum and mercurosum—chemists present will understand what is meant by these terms—so that the white chloride only is in reality comparable with these other chlorides. But no chlorides of copper, mercury, or thallium are known containing less chlorine than the cuprous, mercurous, or thallous chlorides, and thus there is no warrant for believing in a silver chloride containing less chlorine than the white chloride —in other words, the analogy breaks down if we attempt to compare the darkened chloride of silver with the lower chlorides of these other

metals, but is perfectly legitimate if we limit the comparison to the white silver chloride and the other subchlorides. If we compare the four metals from this, the only admissible standpoint, we shall find that the analogy not only does not favour the view that the darkened product of photo-decomposition is silver subchloride, but that it furnishes many strong arguments against this view.

In the first place, the fact that the product of photo-reduction is a highly-coloured compound is at variance with the fact that all the other subchlorides are white. In the next place mercurous chloride is, as I pointed out in the last lecture, resolved by the action of light into mercuric chloride and metal and not into a lower chloride and chlorine. Then again the lower chlorides of mercury, copper, and thallium are perfectly definite salts easily prepared by chemical methods; but they cannot be formed in the presence of oxidizing agents, and that is why it is impossible to believe that the darkened silver compound, which forms under nitric acid, is a subchloride.

It is to be hoped that the time which I have devoted to the consideration of this one salt of silver will not be looked upon as out of proportion to its importance, but the photo-decomposition of the chloride is really a type reaction as far as concerns our present subject. I told you at starting that the object of these lectures was to enable you to see among other things how much we have yet to learn concerning the chemistry of photographic processes, and now at the very outset we find ourselves face to face with a fundamental reaction which cannot be satisfactorily explained. From one point of view, however, this is perhaps rather a fortunate circumstance, because you will perceive that there is yet room for further investigation in this direction. Then again, if you once adequately realize the fact that the equation:—

$$4AgCl = 2Ag_2Cl + Cl_2,$$

does not rest upon an absolutely secure experimental basis, you will be the better prepared to receive the true explanation when it comes,

without that severe shock to the feelings which is generally produced by the upsetting of time-honoured notions. Moreover, as modern photography is so largely dependent on the photo-decomposition of the silver haloids, we had better extract all the information we can from the chloride before proceeding to the other salts.

To resume the argument, I will remind you then that the ground has been to some extent cleared by our having arrived at the conclusion that silver chloride undoubtedly loses chlorine on exposure to light, but that there is no satisfactory evidence that the darkened product contains the subchloride, Ag_2Cl. But whatever may be the chemical composition of this product of photo-decomposition, we may provisionally call it a reduction product, because it contains less chlorine than the unaltered chloride; and to avoid expressing myself dogmatically with respect to the formula of a substance which has never been isolated, I propose throughout these lectures to speak of this and of the analogous compounds simply as reduction products.

Now with reference to the photo-decomposition of silver chloride, it is well known that under ordinary circumstances—that is in the absence of strong reducing (chlorine absorbing) agents—the reaction is a diminishing one, by which I mean to say that the compound does not go on continuously losing chlorine till a darkened reduction product of definite composition is left, but the amount of decomposition becomes smaller and smaller and finally reaches a limit, so that the end result is always a mixture consisting of a large amount of unaltered chloride *plus* a small percentage of reduction product [C]. It is this very circumstance that has made the investigation such a difficult one for the chemist. The quantity of reduction product is so small and it is associated or combined with such a much larger amount of unchanged chloride, that its isolation has baffled all ingenuity. Even if the chloride is exposed in thin films so as to get the maximum amount of photo-decomposition, the difficulty of separating the reduction product from the unaltered chloride without decomposing

the former is a serious obstacle to the practical solution of the problem.

But, it may now be asked, if the darkening of the chloride is not due to the liberation of metallic silver nor to the formation of a sub-chloride, to what chemical change must the discoloration be attributed? It will be necessary at this stage to inquire what other views have been put forward in explanation. Passing over the theory that the change is purely physical, which, for sufficiently obvious reasons, has already been rejected, it may be considered in the first place whether the chloride simply undergoes dissociation under the influence of light. The apparent absence of free metallic silver in the darkened product and the want of evidence as to the existence of a subchloride, render such a view highly improbable. It may be asked in the next place therefore whether the darkened product is really composed only of silver and chlorine, or whether it may not contain oxygen or the elements of water as essential constituents. It must be confessed that in this direction there

is certainly a great want of further experimental investigation. It is known that moisture accelerates the photo-decomposition, but it is not known whether in the total absence of air and moisture the change is altogether arrested. I make this statement with a full knowledge of the numerous experiments which have been made to test this point, but every chemist knows how difficult it is to get substances really pure, and with respect to gases it is only within recent times that we have learnt to appreciate the enormous difficulty of removing the last traces of moisture—I allude of course to the results obtained by Prof. H. B. Dixon in his researches on gaseous explosions. There is a certain amount of evidence that moisture or oxygen or both are essential to the photo-decomposition of silver chloride, and it is for this reason that I have directed attention to the want of further investigation.[1]

[1] According to Abney dry silver chloride sealed up in a Sprengel vacuum does not darken when exposed to light for months. The presence of mercury promotes photo-decomposition. *Recent Advances in Photography*, 1882, p. 19.

That oxygen is essential to the darkening of the chloride was first distinctly announced by the late Robert Hunt[1], and I am glad of the present opportunity of recalling attention to the work of an investigator who has been so recently removed from among us. In connection with the preparation of the present lectures I have frequently had occasion to refer to the writings of this author, and I have been struck with the large amount of carefully performed experimental work which he has left on record. The experiment bearing on the present subject is best described in his own words:—

"The absorption of oxygen, or rather its combination with the decomposing chloride, is proved by another very easy experiment. Some pure chloride of silver was arranged in a bent tube closed at one end, and the other end immersed in a bottle of distilled water. In this state the chloride was exposed for many days to the action of sunshine, during which time it was frequently shaken, for the purpose of exposing

[1] *Researches on Light*, 2nd ed. 1854, p. 80.

the whole of the powder to its influence. As the chloride darkened the water rose into the tube, and it gave a precipitate of chloride of silver on the addition of the nitrate, thus appearing to prove the substitution of oxygen for chlorine under the agency of solar radiation. It was quite evident that some absorption of atmospheric air had taken place."[1]

If we criticize this experiment in the light of modern chemical knowledge, it must be admitted that the proof that the oxygen which disappears is absorbed by the darkening chloride is not perfectly conclusive, because it is possible that the nascent chlorine in the presence of water vapour and under the influence of light may form some oxide of chlorine which dissolves in the water.[2] But in spite of this

[1] A similar experiment is described in *The Art of Photography* by Dr. Halleur. English translation, 1854, p. 76.

[2] It is sometimes asserted that hypochlorous acid is formed when silver chloride is decomposed by light in the presence of water, but the equation usually given, apart from its assumption of the existence of the unknown subchloride, is in the highest degree improbable. This equation is:—

$$4AgCl + H_2O = 2Ag_2Cl + HClO + HCl.$$

objection the experiment is a very suggestive one and is well worthy of further study. At any rate we get a hint that oxygen may be necessary for the darkening of the chloride under the action of light, but whether this element is taken from the air, or whether it is supplied by water vapour taking part in the reaction is not at present manifest.

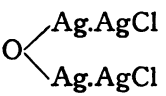
If oxygen, either in the free state or in the

It is well known to chemists that hypochlorous and hydrochloric acids mutually react with the liberation of chlorine:—

$$HClO + HCl = H_2O + Cl_2.$$

The earliest record I can find as to hypochlorous acid being formed is in the report of the British Association Committee of 1859 (B.A. Rep. 1859, p. 107) wherein it is stated that the clear solution (containing silver nitrate) in which silver chloride had become darkened gave a further precipitate of chloride on the addition of sulphurous acid, this being considered as evidence of the presence of an oxide of chlorine in the solution. I have repeated this experiment, but cannot confirm the statement. It is true that sulphurous acid produces a white precipitate, but this dissolves up completely on warming with dilute nitric acid and therefore contains no chloride: not the slightest turbidity was observed in a solution thus treated which had been in contact with silver chloride for more than a month, and exposed with frequent agitation to daylight and sunlight during that time. The same white precipitate is produced on adding sulphurous acid to a solution of silver nitrate, and is no doubt silver sulphite.

form of water vapour, is essential to the photo-decomposition of silver chloride, it is evident that the darkened product must contain some compound of the nature of an oxychloride. It is in this direction that I venture to think we must look for the future solution of the problem of the chemical constitution of the photosalt. This view has been suggested more than once, but it rests at present without rigorous experimental proof. I may state that the subject is undergoing investigation by Dr. W. R. Hodgkinson, and although his results are not yet completed, I believe I shall not be guilty of a breach of confidence if I state on his authority that the darkened product contains an oxychloride of the probable formula, Ag_4OCl_2,[1] or :—



If we appeal to analogy in a legitimate way we certainly do get warrant for believing in

[1] Dr. Hodgkinson has since informed me that he has confirmed this result.

the probability of the foregoing formula. The analogy is supplied by the subsalts of copper and thallium, which are already in the lowest state of chlorination. Both thallous and cuprous chloride are white but become discoloured on exposure to light, the cuprous salt when moist becoming first violet and then brownish black, the change being in all probability due to the formation of an oxychloride [D].

The consideration which has now been given to the photo-chemistry of silver chloride will simplify our work in dealing with the other haloids. The remarks which have been made with respect to the supposed subchloride apply with equal force to the subbromide and subiodide—that is to say we have no evidence that such compounds as Ag_2Br or Ag_2I are formed under the influence of light. Silver bromide darkens on exposure to light and loses bromine, the product finally becoming of a greyish violet, but never as dark as the reduction product of the chloride. As in the case of the latter the presence of bromine absorbents such as silver

nitrate, stannous chloride, or organic compounds, accelerates the photo-decomposition, while such compounds as mercuric, ferric, or stannic chloride retard the decomposition. In the case of silver iodide the discoloration by light is less than with the bromide, and does not take place at all unless some iodine absorbent is present. The pure iodide free from excess of silver nitrate is apparently unchanged by light, but in the presence of silver nitrate or other iodine absorbent it acquires a greenish grey colour.[1] The darkened product is more readily decomposed by nitric acid than the corresponding compound from the bromide.

Before leaving the photo-chemistry of the silver haloids attention must be called—and I regret that time will not permit me to do much more—to the coloured forms of these salts recently

[1] According to Abney (*Treatise on Photography*, 5th ed. p. 24; also Hunt's *Researches on Light*, 2nd ed. p. 98), oxygen is given off under these circumstances; but this is doubtless due to a secondary reaction. We have observed that both silver chloride and bromide when exposed to sunlight under silver nitrate solution give off bubbles of gas, especially when the solution is warmed.

obtained by Carey Lea and described by him under the names of photochloride, photobromide, and photoiodide.[1] Without entering into the details of the various methods of preparing these coloured haloids, I may state that they are produced by reactions such as would tend to give rise to the formation of subsalts (supposing these to exist) in admixture with the normal haloids. The principle concerned, expressed in the briefest terms, is that a silver salt should first be partially reduced by suitable reducing agents, and the product, after being freed from impurities, converted into the haloid by treatment with the necessary acid. Thus the photochloride may be obtained of a red colour and with sufficient rapidity to enable its formation to be shown as a lecture experiment. Taking a solution of silver nitrate I add a solution of common salt in slight excess, and then sufficient ammonia to dissolve up the silver chloride. To the ammoniacal solution ferrous

[1] *Amer. Journ. of Science* for May, June, July, and November, 1887.

sulphate solution is then added and the black precipitate allowed to subside, the clear liquor poured off, and the precipitate washed two or three times by decantation. The liquor is now made acid with dilute sulphuric acid and the precipitate again washed by decantation. On boiling the latter with dilute nitric acid, washing as before, and then boiling with dilute hydrochloric acid, we get this reddish compound in accordance with Carey Lea's statement [E]. I have had some of the other experiments repeated before the lecture and the results are before you [F].

These coloured haloids, which the author calls "photosalts" because he considers them to be identical with the products formed by photo-decomposition, contain less halogen than the normal haloids, and the reasons adduced in support of the view that the latent photographic image is formed of such photosalts appear to be perfectly valid. The discovery is too recent however to enable us to estimate its real significance at present, but I may observe with respect to the chemical composition of these

photosalts that the method adopted for determining this composition is open to precisely those objections which have been urged in a former part of this lecture. By this I mean to say that the deficiency of halogen has been *assumed* to represent the formation of a corresponding amount of subsalt without adequate proof—it may be really due to the existence of an oxyhaloid compound as an essential constituent of the coloured salt.

There is one point in these recent researches which is worthy of a little further consideration, and that is the suggestion that the photosalts are not definite chemical compounds of the reduction product with unaltered haloid, but that the combination is more of the character of a "lake". It is well known to all who have worked practically at chemical analysis that certain precipitates such as barium sulphate, ferric and chromic hydroxides, alumina, &c., have the property of bringing down with them a small quantity of the salts contained in the solution from which they are precipitated. The soluble

salts thus retained cannot be considered to form definite chemical compounds with the precipitates, but the fact that they are very difficult to remove by washing shows that some kind of combination exists. This property is made practical use of in the preparation of those coloured compounds known as "lakes," which consist of some organic colouring matter precipitated in the presence of alumina [G]. In accordance with this view of the nature of the photosalts it has been found that silver chloride also possesses the property of retaining small quantities of other metallic soluble chlorides such as ferric, mercuric, and the chlorides of manganese, cobalt, and nickel, which are not easily washed out of the precipitate. As bearing on the present point it will be of interest to mention that metallic silver can be made to form some kind of physical combination with magnesia, the properties of the metal being so disguised that mercury fails to extract the whole of the silver, even on prolonged amalgamation. The compound in question is simply

formed by precipitating silver nitrate with magnesia, collecting the precipitate, washing, drying, and strongly igniting the mixed oxides of silver and magnesium.[1] From these results it follows that the photosalts may consist of such physical combinations of unaltered haloid with the reduction product, and in the absence of more precise information this is the view of their constitution which most strongly commends itself to the notice of photographic chemists.

[1] Friedheim, Ber. 1888, p. 316.

APPENDIX TO LECTURE II.

A (p. 38).—The following experiments illustrate the point referred to :—No. 1. Silver chloride is prepared by precipitation in the usual way, taking care to use a slight excess of silver nitrate so as to have no free soluble chloride. After being thoroughly washed by decantation (in a 'dark room') the chloride is brought into the lecture room in the flask in which it was prepared and shaken up with distilled water to which a few drops of sulphurous acid solution have been added. Some of the clear liquid is filtered off into a test tube and the flask then placed in the electric beam and kept there with occasional agitation for five minutes, when a second quantity of the liquid is filtered off. The flask is exposed as before for another five minutes and then a third filtrate obtained. The three filtrates are then placed side by side, acidulated with nitric acid, and silver

nitrate added to each: the first remains clear, the second gives a slight, and the third a considerable turbidity, showing the gradual liberation of chlorine from the chloride which at the same time becomes darkened.

No. 2. The old experiment of exposing moist silver chloride to light in one limb of a bent tube, the open end of which dips into a vessel of distilled water, was also shown. The chloride had been exposed for about a week previously in the apparatus figured below :—

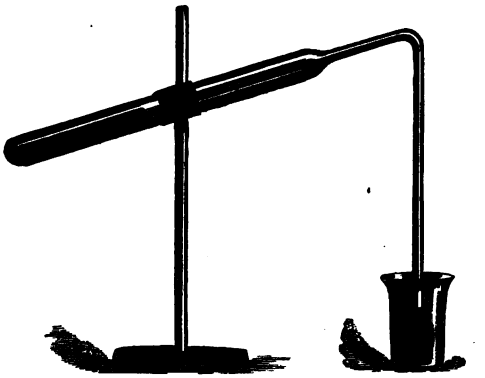


FIG. 1.

The water from the beaker on being tested for chlorine in the usual way gave a distinct precipitate.

No. 3. Some moist silver chloride is placed in

the bottom of a tube and a strip of paper sensitized with potassium iodide and starch suspended above it, the mouth of the tube being closed by a well fitting cork or india-rubber plug. The apparatus is shown in the figure:—

FIG. 2.

On placing the arrangement in the electric beam for about ten minutes the starch paper becomes intensely blue. This gives a most striking lecture demonstration of the liberation of chlorine or of some chlorine containing gas by the action of light.

B (p. 39).—The following illustrations were made use of:—

No. 1. Three tubes were exhibited in which silver chloride (prepared by precipitating silver nitrate with excess of hydrochloric acid and washing by decantation) had been sealed up, (*a*) moist in air; (*b*) dried and in dry air; (*c*) dried and in chlorine. These tubes had been exposed to light some days before the lecture, the chloride in (*a*) being very dark, that in (*b*) less discoloured, and that in (*c*) had remained white.

No. 2. Freshly prepared and washed silver chloride was placed with water in two test tubes, to one of which a few drops of mercuric chloride solution were added. On exposing the two tubes together to the electric light the chloride in the one containing the mercuric salt remains white, while that in the other rapidly darkens.

C (p. 50).—The increase of decomposition of silver chloride with the time of exposure was shown by placing a sheet of paper coated with the chloride in the beam of electric light, and covering up successive portions by means of a black paper screen after exposures of five, ten, and fifteen minutes.

D (p. 57).—The photo-decomposition of cuprous chloride may be shown and makes a most striking lecture demonstration. The two following experiments can be performed before the audience:—

No. 1. Cuprous chloride is prepared by boiling

cupric oxide and scraps of copper foil with strong hydrochloric acid till the solution becomes clear. After being allowed to settle for a few minutes the clear solution is poured into cold water contained in an upright glass cylindrical vessel (gas jar), and the white crystalline cuprous salt immediately settles down to the bottom. The clear liquid is poured off and the precipitate washed once or twice with distilled water by decantation, an operation which takes but little time owing to the rapidity with which the heavy crystalline salt subsides to the bottom. The cylinder is then placed in the beam of electric light when the cuprous chloride towards the light becomes almost black in 5—10 minutes, the side away from the light remaining white.

No. 2. A polished copper plate with a perfectly clean surface is immersed in a strong neutral solution of cupric chloride (prepared by boiling hydrochloric acid with cupric oxide in excess) till a uniform film of a greyish colour is obtained. This is best done in an ordinary photographic dish, in which the solution can be rocked to and fro over the surface of the plate. In about five minutes the plate is removed, washed with water and drained on blotting paper and then exposed, the surface being slightly moist, under a design cut out in black paper, to strong electric light for at

least ten minutes. On removing the black paper the design appears distinctly photographed, the exposed portions being darker than the protected portions. This experiment has been adapted for lecture purposes from Priwoznik (Ding. Poly. Journ. Vol. ccxxi., p. 38).

E (p. 60).—The experiment was shown in the way described in the text. It requires about 8—10 minutes for its completion.

F (p. 60).—A specimen of the rich purple photobromide was exhibited, prepared according to Carey Lea's directions which are here subjoined :— 3 grams silver nitrate are dissolved in 100 c.c. water and ammonia added so as just to redissolve the precipitate. The ammoniacal silver solution is poured into 100 c.c. water containing 6 grams of ferrous sulphate in solution. To the mixed solutions add 2 grams of pure caustic soda dissolved in 25 c.c. of water, allow to stand for a short time and then add $2\frac{1}{2}$ grams of potassium bromide dissolved in a little water. Make the mixture acid with dilute sulphuric acid, wash the residue thoroughly by decantation, and warm (it is safer not to boil) with dilute nitric acid (1·36 sp. gr. acid with 5 times its bulk of water).

G (p. 62).—The formation of a lake can be strikingly shown by taking a large flask containing a hot solution of ammonium alizarate (prepared by

adding commercial alizarine paste to the water and then a few drops of ammonia), and then adding to the hot solution, which is of a deep purple colour, first some sodium carbonate solution and then a solution of alum. The coloured lake is at once precipitated and on pouring the contents of the flask on to a filter the solution comes through quite colourless.

LECTURE III.

Theory of the Action of Sensitizers.—The Colour Change of the Silver Haloids not a Quantitative Indication of their Relative Sensitiveness to Light.—Foundation of Modern Photography.—Wedgwood, Davy, and Fox Talbot.—Joseph Nicéphore Niepce and Daguerre.—The Collodion Wet Plate Process.—Collodion Dry Plates.

IN the last lecture we devoted ourselves to the photo-chemistry of the silver haloids without special reference to their photographic utility, and without taking into consideration any other circumstance than that they are decomposed by the action of light with the liberation of a portion of their halogen. It appeared incidentally that this photo-decomposition was accelerated by the presence of halogen absorbents and that in the

case of the iodide some such substance was absolutely essential in order to render the product of decomposition visible. We have next to inquire a little more closely into the theoretical bearing of this principle in order that we may approach the practical part of our subject with due preparation. We have in fact arrived at the border-land between photo-chemistry and photographic chemistry, and it will be advisable to commence with a comparative study of the three haloids.

From the fact that halogen absorbents facilitate or in some cases are absolutely indispensable for the photo-decomposition of a silver haloid, we may deduce a general principle which can be expressed in abstract terms and which will be useful for further progress. If we say that a substance is composed of the elements A and B we simply mean that the compound A B is in a state of chemical equilibrium—that it is stable under ordinary conditions of temperature. If energy be supplied from external sources either in the form of heat or electricity, or, in some instances, light, the equilibrium tends to become upset, that is to say the

compound tends to become resolved into A+B. Now some compounds have the equilibrium of their internal chemical forces more readily upset by one form of energy, and others by some different kind of energy. Thus the silver haloids which are so readily decomposed by light are very stable under the influence of heat. Why this should be the case—why some compounds should be susceptible to the influence of one form of energy and others to another form of energy—is a question of molecular physics into which we cannot now enter. The compounds which the photographer has to deal with are of course those which are especially susceptible to the action of light.

The first point in connection with the general principle which I am now about to develop is one of considerable importance, if only from the circumstance that it is apt to be overlooked, to say nothing of its having an important bearing on photographic operations. The point is that we are liable to estimate the action of light upon a compound entirely by the amount of visible colour change which it undergoes. In consequence of

this we may over-estimate the sensitiveness of some compounds and under-estimate that of others, or we may fail altogether to recognize that a compound is acted upon by light simply because it shows no change in colour. But the circumstance that the product of photo-decomposition is a highly coloured substance is, after all, only a chemico-optical accident, and we must be careful therefore to bear in mind that the amount of colour change is no absolute measure of the amount of decomposition—that is, of the relative sensitiveness of the different compounds which may be compared with respect to the action of light upon them.

Supposing then we have a compound A B capable of being resolved by light into A+B, it may be regarded as a general principle that the presence of another substance C capable of forming the compound A C with A or B C with B facilitates the photo-decomposition; in other words the *sensitiveness* of A B is increased, or the system A B+C is more sensitive to light than A B alone, for which reason we speak of the substance C as a *sensitizer*. It is of interest to bear in mind that the sensitizer

may be a simple or compound body and that it may be in any state of physical aggregation, *i.e.* either gaseous, liquid, or solid. To give a few examples:—paper acts as a sensitizer towards many salts, such as silver nitrate, ferric chloride, and potassium dichromate; alcohol and ether act as sensitizers towards such salts as the ferric, auric, and platinic chlorides. As an example of a gaseous sensitizer hydrogen accelerates the photo-decomposition of silver chloride.[1]

The foregoing remarks will suffice to make clear the true function of a sensitizer, and the next point to which I wish to call your attention is an extension of the general principle which has some photographic importance. The sensitiveness of the system A B+C is not only greater than that of AB alone, but its sensitiveness is a function of the affinity of C for A or B. Let me illustrate this point more fully by an appeal to a special case. Silver chloride in the presence of silver nitrate is more sensitive to light than silver chloride alone because silver nitrate is a chlorine absorbent. On

[1] Hunt's *Researches on Light*, 2nd ed. p. 78.

the other hand, as I showed in the last lecture, stannic or mercuric chloride retards the photo-decomposition of silver chloride because these salts not only have no affinity for chlorine, but they tend to prevent the liberation of that element. If we compare silver chloride moistened with (1) silver nitrate solution, (2) with water, and (3) with a solution of stannic chloride, we should say that the system $AgCl+AgNO_3$ is more sensitive than the system $AgCl+H_2O$, and that the latter is more sensitive than the system $AgCl+SnCl_4$, because chlorine readily enters into reaction with $AgNO_3$, less readily with H_2O, and not at all with $SnCl_4$ [A].

Bearing these considerations in mind we shall now find ourselves in a better position to deal with the comparative action of light upon the three silver haloids. If we expose three strips of paper coated respectively with the chloride, bromide, and iodide of silver, we shall find that with equal exposure the chloride darkens considerably, the bromide slightly, and the iodide not at all [B]. Experiences of this kind formerly gave rise to the

impression that the chloride is more sensitive to light than the bromide and the latter more sensitive than the iodide. The papers used in this experiment have not been specially sensitized—they have been prepared in each case with an excess of soluble alkaline haloid so as to insure the absence of free silver nitrate. The same sensitizer, paper and moisture, is present in each case. The question now before us is: How are the results to be interpreted?

In working out the answer to this question we shall be enabled to apply the general principles which have already been laid down. You are prepared for the possibility that the amount of discoloration may not be a measure of the relative sensitiveness of the three haloids, and you are aware that the sensitiveness of the salts depends also upon the nature of the sensitizer. The first idea that suggests itself therefore is whether the relative sensitiveness of the silver haloids could not be varied at pleasure by a proper selection of sensitizers. It will be instructive to put this idea into an abstract form:—

The system A B+C is more or less sensitive to light according to the affinity C for one of the constituents, say B. If we have another sensitive compound, D E, and use the same sensitizer C, the sensitiveness of the system D E+C may be fairly compared with that of A B+C, because we have then only to consider the relative stability of A B and D E and the relative affinities of B and E for the same substance C. If the affinity of C for B and E is equal, then the sensitiveness of the compounds A B and D E is measured by the amount of decomposition which they undergo with the same amount of exposure to light. On the other hand if A B and D E are equally sensitive, their relative sensitiveness might be varied by selecting some other sensitizer F having different degrees of affinity for B and E. In this case we have for consideration the four systems :—

AB + C . . . . . (1)
AB + F . . . . . (2)
DE + C . . . . . (3)
DE + F . . . . . (4)

If the affinity of C for B is greater than that of F for B, then (1) will be more sensitive than (2). If the affinity of C for B is less than that of F for B, then the order of sensitiveness will be reversed. It is quite unnecessary to go on ringing the changes on all the systems, but you will readily gather that even if we had two compounds A B and D E, of which the first was absolutely more stable than the second, we might equalize or even reverse their relative sensitiveness by selecting a sensitizer which had a much greater affinity for B than for E.

Now we may descend once more from the general to the special and consider a particular instance. In order not to complicate matters too much we will limit ourselves to two of the haloids only, say the bromide and iodide. If we had a sensitizer which entered into reaction with bromine more readily than with iodine we should find the bromide more sensitive than the iodide; if on the other hand we had a substance capable of fixing iodine more readily than bromine we should find the order of sensitiveness reversed. I may

mention incidentally that this state of affairs is actually seen in photographic processes. I do not mean to imply that the causes are quite so simple as may appear from the reasoning, but there is no doubt that the main principle is of the nature indicated. Thus it has been found that in some processes the iodide is more sensitive than the bromide, while in other processes the bromide has the advantage.

In considering the comparative action of light upon the three silver haloids it is therefore evident that no absolute meaning can be attached to the term "sensitiveness" unless we specify the sensitizer used, and even when this is done our ignorance of the degree of affinity between the halogen and the sensitizer often renders it very difficult to predict which sensitizer is the best adapted for any particular haloid. If we take three strips of paper coated with the three haloids, paint on each a stripe of the same sensitizing solution and expose all three for the same time to the action of light, we shall find the same order of darkening as with the unsensitized papers—the

chloride darkens most and the iodide least. The only effect of the sensitizer is to accelerate the discoloration in all three cases [C]. From such an experiment we gain no information as to the relative instability of the three haloids—the degree of darkening is no measure of the amount of decomposition. There may be just as much or more of the bromide decomposed than there is of the chloride, only the oxychloride, or whatever the product of decomposition may be, being more highly coloured than the oxybromide, makes the greater show, and the same comparison can be made between the bromide and iodide. In order to make the comparison between the haloids perfectly fair, we must not only disregard the amount of discoloration but the sensitizer must have the same affinity for the three halogens, or different sensitizers must be chosen, so that the halogen-absorbing power is the same in all three cases. Such conditions would be very difficult to realize in practice, but the conclusion which may be drawn from this discussion of the comparative action of light upon the three haloids is that for

photographic purposes the order of sensitiveness bears no relationship to the order of darkening and may be in fact quite the reverse of this order. If we apply physical considerations we shall see that there is every reason for believing that the iodide is the least stable and the chloride the most stable, the heats of formation of the three haloids being :—

Ag, Cl	29,380	gram units.
Ag, Br	22,700	„ „
Ag, I	13,800	„ „

But although we are now able to look upon the degree of photo-discoloration of a silver haloid as a character quite distinct from its sensitiveness in the photographic sense, it can be readily understood that the earliest efforts were directed to that compound which undergoes the greatest perceptible change on exposure to light. This brings us to the beginning of the art of photography in the year 1802, when Thomas Wedgwood and Humphry Davy published an account of a process for copying pictures

painted on glass or profiles cast by a strong light, by means of paper or leather impregnated with a solution of silver nitrate or coated with the chloride. The delineations thus produced were of course but transitory because, on exposure to light, the undarkened portions of the design also darkened and the picture gradually disappeared. No fixing agent had at that time been discovered and Davy adds :—"Nothing but a method of preventing the unshaded parts of the delineation from being coloured by exposure to the day is wanting to render this process as useful as it is elegant."

A step in the direction indicated by Davy was made by Fox Talbot in 1839. In a communication to the Royal Society this experimenter described a process for coating paper with silver chloride, and for obtaining impressions of objects placed in contact with the prepared surface by exposure to light. The advance upon the experiments of Wedgwood and Davy was however but slight because the fixing agent used was very imperfect in its action. This xing agent was a solution of common salt, the fficiency depending upon the solvent action of

sodium chloride upon those portions of the silver chloride unacted upon by light [D]. It is hardly necessary to say that these earliest Talbotypes were of no permanent value owing to the imperfect removal of the unaltered silver salt; nevertheless the process has a certain historical importance because we have in this discovery the first production of what in its modern development we know as a silver print. It will be of interest to add that the fixing agent now in general use, sodium thiosulphate, was known to Sir John Herschel as far back as 1819, and the application of this salt was described by him in 1839 in a paper to the Royal Society, read shortly after that by Fox Talbot.

Although it is no part of my scheme to attempt to give you a complete history of photography, it will be advantageous at this stage to keep to the historical order, and in so doing it becomes only a matter of duty to name the different investigators who have helped to develop the art to its present state of utility. The processes of Wedgwood and Davy and of Fox Talbot, with which we have

hitherto been dealing, were all based on the visible discoloration of a silver salt under the influence of light, and although such prepared surfaces were well adapted for the production of prints they were not sufficiently sensitive to record the image formed by a lens—that is the camera picture with all its gradations of light and shade. The great desideratum which the early experimenters had in view was the fixation of this camera image, and all their efforts were directed to the discovery of some substance sufficiently sensitive for the purpose. In a former lecture I called attention to the experiments of Joseph Nicéphore Niepce of Châlons, who was the first to fix a camera picture on a sensitive surface of bitumen. This investigator made his process known in 1829, after fifteen years' work upon various substances. Five years previous to this date another French experimenter, the painter Daguerre, had commenced work upon photography, and in 1829 he and Niepce entered into partnership and prosecuted their experiments conjointly. Niepce died in 1833, and Daguerre continued the experiments upon iodized silver plates, which had

been commenced during his partnership, the outcome of these researches being the process known as the Daguerreotype, which was announced in 1839, a year of memorable importance in the history of photography because this was the first practical application of a silver compound to the fixation of a picture formed by a lens in the camera.

The system of Daguerre has now passed out of the domain of practical photography, but we shall see subsequently that this old process still has much to teach us. From our present point of view the method is of the greatest importance, because it brings us into contact with a kind of photo-chemical action which may, at first sight, appear of quite a different order to any of the actions with which we have hitherto been concerned. The great principle revealed by this discovery was that the photo-reduction of silver iodide could take place without any visible discoloration of the surface—that an invisible image could be formed by a comparatively short exposure, the picture only becoming visible when submitted to a subsequent operation of development. All the photographic processes which

have been invented since the time of Daguerre take their departure from this discovery of the formation of an invisible image and its development by appropriate treatment.

I now propose to pass briefly in review the more important of the methods which have been or still are of practical utility—not with the object of giving detailed instruction in the working of the numerous processes, for this could not be properly done in a course of lectures, and the necessary information can be obtained from the various works dealing with practical photography. It is my object rather to give a sufficiently distinct general idea of the nature of the operations performed to enable the chemical principles underlying them to be understood as far as permitted by our present state of knowledge. This review must necessarily be brief, and it will perhaps be best to deal with the processes up to the first stage only, *i.e.* the formation of the invisible image. The subsequent operations of development, intensification, fixing, &c., will be better dealt with separately because we can make their study a comparative

one, a method of treatment which will the better enable us to extract any general principles that may underlie them.

Commencing with the Daguerreotype, we have a sensitive surface prepared by exposing a highly polished plate of silver (or silvered copper) to the vapour of iodine and bromine alternately, so as to obtain a film of the bromo-iodide of silver. The proper degree of sensitiveness is judged by the colour of the surface, and this requires much experience. In the original process iodine alone was used, but with pure silver iodide an exposure of from fifteen to twenty minutes was necessary, so that portraiture was hardly practicable in the early days of the process. It was found by Goddard in 1840 that the sensitiveness was considerably increased by the use of bromine in conjunction with iodine, and a good Daguerreotype plate can now be prepared of about the same degree of sensitiveness as a wet collodion plate.

The early efforts of Fox Talbot have already been alluded to. Shortly after the introduction of the Daguerreotype this experimenter made known

an improvement upon his former process, in which the sensitized paper was coated with silver iodide instead of the chloride, and a mixture of gallic acid and silver nitrate was used as a developer. It may be mentioned incidentally that the discovery of this developer is said to be due to the Rev. J. B. Reade. The complete method of obtaining a picture by exposing paper coated with silver iodide and sensitized with silver nitrate and gallic acid, developing with the same materials and fixing by sodium thiosulphate, was patented by Fox Talbot in 1841, the process being known as the Calotype. Improvements were subsequently made by many workers; the sensitiveness of the paper was increased by the use of a mixture of bromide and iodide instead of silver iodide alone, this modification being due to Blanquart-Evrard of Lille.

The advantages of these paper processes over the Daguerreotype were that in the first place the picture was more artistic, being on a dull paper surface instead of on a polished metallic mirror which had to be viewed at a particular angle, and

in the next place the paper photographs could be used as negatives, from which a large number of positive prints could be obtained, the Daguerreotype plate being of course unsuited for this purpose. One drawback to these processes was the want of definition and the frequent irregularities in the prints, due to the coarseness of the paper fibre and the consequent inequalities in the transparency of the paper negative. To obviate this, Blanquart-Evrard proposed in 1848 to improve the paper negative by coating it with albumen, and in 1849 Le Gray employed gelatine for the same purpose. This last experimenter also introduced the method of waxing the Calotype negatives, and by this means rendered them more transparent and uniform. Through the kindness of Mr. John Spiller, who has been associated with photography from its earliest days, I am enabled to show you some waxed paper negatives, and the prints obtained from them, which are of considerable historical interest, being the work of Fox Talbot himself.

The defects in the paper negatives which have

just been alluded to led as a natural result to attempts to obtain negatives on a surface of greater uniformity and transparency, a glass plate being of course the most suitable for this purpose. It appears that a successful photograph on a film of silver chloride deposited on glass (by subsidence) was taken as far back as 1843 by Sir John Herschel, but the difficulty of obtaining films by this method was too great to enable the process to become generally practicable. The first successful introduction of glass plate photography is due to Niepce de St. Victor, nephew of the older Niepce, who about the year 1847 tried various substances for coating the plate, the first of these being starch paste which was soon replaced by albumen from the whites of eggs. The process, known as the Niepceotype after its discoverer, was carried out by coating the plate with albumen previously mixed with a solution of potassium iodide and, when dry, the film was sensitized by immersion in a silver nitrate bath, a layer of silver iodide on an albumen substratum being thus formed. The prints from these albumenized glass negatives were a consider-

able improvement upon those obtained from Calotype waxed paper negatives. It will be of interest to mention that in 1849 Blanquart-Evrard showed that these plates could also be employed when dry, so that we have here the first hint at dry plate photography. Numerous modifications and improvements have been made from time to time in the original process of Niepce, but these do not bring us into contact with any essentially new principles.

The next advance in photography brings us to the use of collodion as a substratum for the silver haloid instead of albumen. The employment of this material was first suggested by Gustav le Gray in 1850 and was made known in a practicable form by Scott Archer in 1851. To attempt anything approaching a complete description of this process would necessitate more than an entire lecture and would moreover take us beyond our present limits of treatment. It is no doubt well known to all here that till within the last few years the collodion process was the only one which could claim to be in general use by photographers. I will endeavour

to compress a concise account of the main features of the process into the shortest possible space.

Collodion is prepared by dissolving certain nitrated products obtained from cellulose in a mixture of alcohol and ether. The cellulose is employed in the form of cleansed cotton wool and is nitrated by means of a mixture of nitric and sulphuric acids of appropriate strength. Gun-cotton, which is the product of the extreme nitration of cellulose, was discovered by Schönbein in 1846. This compound is cellulose hexanitrate, $C_{12}H_{14}O_{10}(O.NO_2)_6$, and is insoluble in alcohol-ether, the lower nitrates only being dissolved by these solvents. By stopping the nitration short of the production of gun-cotton, which can be done by employing a mixture of nitric and sulphuric acids with a little water, the trinitrate, $C_{12}H_{17}O_{10}(O.NO_2)_3$ and tetranitrate, $C_{12}H_{16}O_{10}(O.NO_2)_4$, are formed and these possess the necessary solubility, constituting what is known as collodion pyroxylin. In addition to this difference in solubility, gun-cotton is, as you know, much more inflammable and burns with greater velocity than collodion pyroxylin [E]. It

will be well to mention here in passing that neither gun-cotton nor the soluble pyroxylin are nitro-derivatives in the sense known to chemists, but are organic nitrates of the type of ethyl nitrate, $C_2H_5.O.NO_2$, or the so-called nitro-glycerin which is glyceryl trinitrate, $C_3H_5(O.NO_2)_3$. I have thought it desirable to mention this because in many works on photographic chemistry the formulæ are written as though the pyroxylins were true nitro-derivatives.

When collodion is poured on to the surface of a perfectly clean glass plate, the alcohol and ether evaporate rapidly and leave a beautifully uniform transparent film of pyroxylin which adheres firmly to the glass. In order to prepare the photographically sensitive surface, the collodion is "salted" by dissolving in it some soluble iodide or bromide or a mixture of the two. The salts usually employed are ammonium or cadmium iodide and cadmium bromide, the coated plate being sensitized by immersion in a bath of silver nitrate which reacts with the bromide or iodide in the film,

giving a layer of silver bromide or iodide by double decomposition :—

$$NH_4I + AgNO_3 = AgI + NH_4NO_3$$
$$CdBr_2 + 2AgNO_3 = 2AgBr + Cd(NO_3)_2$$

The plate is exposed in a moist state, that is to say, covered with a film of adhering silver nitrate solution. It is important to bear this condition in mind because it is this film of silver nitrate solution that is essential as a sensitizer ; the collodion itself, having no halogen absorbing power, has no sensitizing action [F].

The inconveniences of the wet collodion process are sufficiently well known to all who have worked it. We need only consider the cumbrous equipment required for field work and the difficulties of carrying about and working in hot climates with a solution containing ether. Soon after the introduction of the collodion wet plate process the first attempt to prepare collodion dry plates was made by Taupenot in 1855, and this process was ultimately developed through various stages into a

really useful method in 1861 by the late Col. Russell. It must suffice here to point out the principles concerned in this most distinct advance in photographic methods.

The object of dry plate photography is to furnish a sensitive film which can be kept till required for use, and which is at any time ready for exposure without having to undergo the operations of coating and sensitizing immediately before placing in the camera. The practical difficulty which had in the first place to be met was the tendency of the collodion film to peel off the plate when dry, or when submitted to the operations requisite for dry plate development. Some substratum which holds the film firmly to the glass is therefore the first requirement. In practice the plate is first coated with albumen or gelatine or with a film of india-rubber by pouring a solution of the latter substance in benzene or chloroform over the surface of the glass and allowing the solvent to evaporate. When the substratum is dry the plate is coated with salted collodion and sensitized by

immersion in a silver nitrate bath in the usual way. Up to this point the operations may be regarded as leading to the production of a wet collodion plate with a film supported on a substratum of albumen, gelatine, or india-rubber. But now the plate undergoes further treatment and a little explanation will make clear the principles concerned in the subsequent operation.

If the plate were allowed to dry after being taken out of the bath, the silver nitrate in the adherent film would crystallize as it dried and, in so doing, would disintegrate or freckle the surface of the silver haloid so that the photographic efficiency of the latter would be completely destroyed. The excess of silver nitrate is therefore removed by washing and, from what has already been said in connection with the wet plate collodion process, you will readily understand that in washing out the excess of silver nitrate we practically destroy the sensitiveness of the plate. The next operation therefore is to coat the surface of the film with some substance which will restore the sensitiveness—that is with some

substance which plays the part of the silver nitrate film in the wet process and which retains this function after drying. Such substances as these are known technically as "preservatives" and in one sense they play this part inasmuch as they preserve the sensitive surface from immediate contact with the air, much after the manner of a varnish.

In the early days of dry plate photography all kinds of substances were tried as preservatives, and on looking back into this chapter of the history of the art we find a collection of formulæ which are amusingly grotesque. I need only remind you of the tea, coffee, gum and beer processes. Other preservatives are albumen, gallic acid, and tannin, the latter being of interest as the substance first used successfully by Col. Russell in the preparation of dry plates. All these substances are organic sensitizers, their sensitizing action being due to their faculty of absorbing the free halogen [G]. It remains only to explain that the preservative is applied to the surface of the plate after the removal of the

silver nitrate, the excess of preservative solution being drained off and the plate being then allowed to dry. Preservatives which retain a slight amount of moisture necessarily give the best results as far as regards sensitiveness, because in the first place water itself is to some extent a sensitizer and, in the next place, a moist sensitizer is likely to be in more perfect contact with the silver haloid of the sensitive film.

APPENDIX TO LECTURE III.

A (p. 76).—The points referred to were illustrated by taking a sheet of paper coated with silver chloride and painting on it two stripes, (1) with a solution of silver nitrate, and (2) with a solution of stannic chloride. On exposing to the electric light for a few minutes the ground-colour darkens, the stripe (1) becomes darker than the ground-colour and the stripe (2) remains white. The paper is prepared with excess of sodium chloride so as to contain no free silver nitrate.

B (p. 76).—The papers coated with the haloids were fastened on a board and all exposed for the same time to the electric light.

C (p. 81).—The last experiment was repeated after a stripe of a solution of silver nitrate had been painted on each of the three strips. The excess of silver nitrate solution should be removed by clean blotting paper.

D (p. 84).—The solubility of silver chloride in a solution of sodium chloride is easily shown by boiling some freshly precipitated chloride with excess of strong brine and pouring the clear solution into cold water when the dissolved chloride is reprecipitated.

E (p. 93).—The difference in the combustibility of gun-cotton and collodion pyroxylin can be shown by placing a loose piece of each on the top of a little heap of rather fine-grained gunpowder. The gun-cotton on ignition simply scatters the powder, while the slower burning pyroxylin explodes the latter. This experiment requires some dexterity.

F (p. 95).—A glass plate is coated with salted collodion and sensitized in a silver nitrate bath in the usual way in "non-actinic" light. On removal from the bath one half of the plate is immersed for a few seconds in a solution of potassium iodide and, after washing slightly, a brief exposure is given to diffused (electric) light. On developing by iron developer the portion of the plate from which the excess of silver nitrate had been removed by immersion in the potassium iodide remains white, while the other half rapidly darkens.

G (p. 98).—The action of an organic sensitizer can be shown by coating and sensitizing a wet collodion plate in "non-actinic" light in the usual

way. After removal from the bath the plate is washed in a stream of water till free from silver nitrate, the excess of water drained off on blotting paper, and a design painted on the surface of the plate with a brush moistened with a solution of gallic acid thickened with a little gum. The plate is then exposed to the electric light for a few seconds, washed, and developed (by iron or ferrous oxalate developer) in the usual manner, when the design appears darker than the background.

LECTURE IV.

Emulsion Photography.—Collodion Emulsions.—Gelatine Emulsions.—The Process of Ripening.—Different States of Physical Aggregation of Silver Bromide.—Extreme Sensitiveness of Gelatino-Bromide Emulsion.—Recent Applications of Modern Dry Plates.

THE photographic processes briefly reviewed in the last lecture belong now to the historical portion of the subject, but there is a thread of continuity running through them which enables us to follow their development in a manner which is of the highest interest for those who take pleasure in studying the evolution of scientific discovery. It would lead me too far astray to attempt such treatment on the present occasion and we must commence at once with the latest methods of dry plate photography, the legitimate offspring

of the collodion dry plate processes last described. The collodion dry plates possessed all the advantages expected of them as far as regards facility of transport and of manipulation, but they failed in sensitiveness and, till their manufacture was properly understood, were apparently capricious in their action. From a chemical point of view we know what lack of sensitiveness means in this case—it means that the so-called preservatives have not the same power of absorbing the halogen liberated by the action of light as is possessed by a sensitizer such as the silver nitrate film of the wet plate process.

The working of collodion dry plates was considerably facilitated by the introduction of alkaline development in 1862 by Col. Russell, a subject to which we shall have occasion to return. But even at their best these dry plates left much to be desired in the way of sensitiveness. The next efforts of photographic experimenters were directed to the production of silver haloids in an extremely fine state of division suspended in some viscid sensitizing medium which could be spread

over the surface of the plate and there allowed to dry. The development of this idea brings us down to the photography of the present, *i.e.* to emulsion photography.

As with so many other useful inventions, we find that the germ of this discovery came into existence long before it bore fruit. As far back as 1853 Gaudin proposed to use the silver haloids in the form of emulsions, and in 1861 he gave details of his experiments. Three years later the first successful emulsion process was made known by Bolton and Sayce, who used silver bromide emulsified in collodion; and in 1865 a collodio-chloride emulsion for printing purposes was described by Wharton Simpson. I must now attempt to give a brief account of the preparation of these emulsions, and the remarks which I felt it incumbent to make when dealing with the wet collodion process must be repeated here with tenfold meaning; for if that process could occupy an entire lecture for its description, the emulsion processes, owing to their multiplicity and the immense amount of practical detail

connected with their working, would demand a whole course of lectures. But you must fully realize by this time that I am not dealing with photographic manipulation, and I shall be obliged to treat of this branch of the subject only in a very general way.

To prepare a collodion emulsion the silver haloid must be precipitated in the collodion itself. There are of course several ways of doing this, but the one general principle underlying them all is that the silver nitrate and the haloid salt with which it reacts should be brought together in the presence of a solvent in which the collodion is itself soluble. Alcohol is the solvent which meets these requirements, and if we dissolve in this liquid some haloid salt capable of dissolving therein and salt the collodion with this solution, we can then add an alcoholic solution of silver nitrate and thus precipitate the silver haloid in the required state of subdivision in the collodion, wherein it remains suspended owing to the viscosity of the medium. Of the silver haloids the bromide appears to lend itself most

readily to this process of emulsifying, and collodio-bromide emulsions are therefore the more generally prepared. As the soluble bromide that of zinc or cadmium is usually employed, the necessary quantity of this salt dissolved in alcohol being added to the collodion and then the alcoholic solution of silver nitrate is gradually poured in, the mixture being briskly agitated after each addition. When the whole of the silver nitrate has been added the emulsion is allowed to stand for some time to ripen, a process which will occupy our attention again later on. It is needless to say that these operations are conducted in red or "non-actinic" light [A].

So far the rationale of the process is simple enough—at least as far as the chemistry is concerned—but the emulsion is by no means ready for use at this stage. Consider for a moment what has been said with regard to the necessity for a sensitizer in the wet collodion process, and let us ask whether there is any sensitizer present in the emulsion prepared in the manner described. It is evident that the only substance capable

of performing this function is the silver nitrate, and it might be imagined that if the quantities of this salt and of the zinc bromide were so adjusted as to leave a slight excess of the nitrate over and above the quantity indicated by the equation—

$$ZnBr_2 + 2AgNO_3 = 2AgBr + Zn(NO_3)_2,$$

all the conditions necessary for sensitiveness would be met. But this plan is unfortunately impracticable, and a little consideration will make clear the reason.

The emulsion, at the stage where we left it, contains in addition to the silver haloid and the pyroxylin, the excess of silver nitrate and the zinc nitrate formed by double decomposition. If a plate were coated with this mixture the soluble salts would crystallize as the film dried and would thus disintegrate and destroy the photographic surface. To render the emulsion fit for use it is therefore washed with water in order to remove the soluble salts, and this is

done either on the plate itself after coating, or the emulsion is washed in mass. It is sometimes customary to speak of these two kinds of emulsions as "washed" and "unwashed," but this is misleading because they are both washed, the latter on the plate after coating and the former in bulk after preparation. It would be better to describe the emulsion as either *film-washed* or *mass-washed.*

The preparation of a collodion emulsion plate by film-washing is a comparatively simple operation. After the plate has been coated with the emulsion the latter is allowed to set and then, before the salts have time to crystallize, the plate is immersed in water till these soluble salts have all diffused out. It might be expected that by thus washing out the soluble salts the sensitiveness of the film would be seriously impaired owing to the removal of free silver nitrate. There is no doubt that the sensitiveness is diminished by this treatment, but it is not altogether destroyed because, in making the emulsion, the quantities are so adjusted as to have an excess

of silver nitrate, and when silver bromide is precipitated under these conditions it is always more sensitive than when formed in the presence of an excess of the soluble bromide. The different sensitiveness of the bromide under these two modes of preparation is no doubt due to the retention of a trace of silver nitrate when an excess of that salt is present, just in the same way that silver chloride retains traces of other soluble chlorides. After washing the emulsion-coated plate in the manner indicated, the sensitiveness is therefore found to be sufficient for photographic purposes. It is customary to coat the washed plate with some organic preservative before drying, but it is stated by some authorities that, in the case of collodio-bromide emulsion prepared with excess of silver nitrate, the sensitiveness is not increased by the preservative. In other words, the retained trace of silver nitrate is a better sensitizer than the preservative, the latter playing no part in this kind of emulsion beyond the protection of the film from atmospheric influence.

When silver bromide has been emulsified in collodion in the manner described it takes a certain time to acquire its maximum degree of sensitiveness, the period of so called "ripening" varying from 8 to 24 hours according to the soluble bromide used as a precipitant, the quality of the collodion, &c. If the emulsion is kept too long it loses in sensitiveness, the silver bromide particles become denser and tend to settle out of the medium, and the photographic efficiency is destroyed. Now this behaviour of the silver haloid in an emulsion is of particular importance to us at the present moment, because this is the first hint we get that the physical state of aggregation may have a determining influence upon the sensitiveness of the bromide. There seems to be a critical point in the state of molecular aggregation of the silver haloid. We shall have much more to do with this ripening process hereafter, but you will readily gather that as a practical outcome of this property the stock of emulsion must be used as soon as possible after it has ripened, and

this is one of the disadvantages of film-washing.

To prepare an emulsion by mass-washing the silver haloid is precipitated in the collodion as before, using either an excess of silver nitrate or an excess of soluble haloid according to the character of the emulsion required. After being allowed to ripen the alcohol and ether are evaporated or distilled off, and the semi-gelatinous emulsion washed by being allowed to remain under water which is frequently poured off and renewed. The soluble crystalline salts are thus removed, and the washed emulsion is freed from water by being allowed to dry in the air spontaneously, by heating on a water-bath, or by being washed with alcohol. The emulsion may at this stage be regarded as consisting practically of a dried silver haloid pyroxylin jelly, and to prepare it for use all that is necessary is to redissolve in the requisite amount of alcohol and ether, coat the plate in the usual way, apply the preservative and dry. The advantage of mass-washing is that

a large quantity of emulsion can be prepared at one operation and may be kept without deterioration till required for use.

The collodion emulsion processes are now more of historical than of practical interest because, as you are aware, they have been displaced by gelatine emulsions which greatly transcend them in sensitiveness. I have dealt with the collodion emulsion in some detail because it was the first emulsion process practically introduced, and we have been enabled to get out of it a good general idea of the principle of emulsification, although there are necessarily many points which I have been obliged to pass over. A collodion emulsion plate, even under the most favourable circumstances, can seldom be made as sensitive as a collodion wet plate, whereas a gelatine emulsion plate may have from ten to one hundred times the sensitiveness of a collodio-bromide emulsion plate. The reasons for this increased sensitiveness of gelatine emulsion will appear in due course, but we have first to consider the process itself.

The use of gelatine as a vehicle was suggested by Gaudin in 1853; but the development of the modern process dates from the year 1871, when Dr. R. L. Maddox made known the practical details of the method of preparing a gelatino-bromide emulsion. Of the chemistry of gelatine but little is at present known. It is a nitrogenous animal substance extracted by boiling from bone cartilage, sinew, connective tissue, and skin. It appears to be resolvable into two compounds, one derived from the unhardened cartilage and called chondrin, and the other derived from the hardened cartilage known as glutin. The latter substance constitutes the chief part of the purer forms of gelatine used by the photographer.

It will be advisable to give here a short account of those properties of gelatine which are connected with its use as a vehicle for the silver haloid emulsion. When allowed to remain in contact with cold water, gelatine swells and absorbs a considerable quantity of the latter; if warmed the substance gradually forms a solution, the

latter solidifying on cooling to a gelatinous mass more or less firm in consistency according to the quantity of water used. Eder states that a good specimen should give a firm jelly when a four per cent. solution is cooled to 20° C. It is this property of gelatinising which renders gelatine available for the preparation of emulsions; it confers upon the water in which it is dissolved the necessary degree of viscosity for keeping the finely divided silver haloid in suspension. Moist gelatine cannot be long kept without undergoing decomposition; chemical changes soon begin to take place even at ordinary temperatures and still more rapidly on heating. The time when decomposition sets in depends much upon the quality of the gelatine, but an average high quality sample, which is usually slightly acid at first, becomes alkaline and begins to evolve ammonia after ten days or so. Inferior kinds, which are alkaline to start with, may show indications of the production of ammonia after three or four days.

As a point of practical importance it should be mentioned that the decomposition of the gelatine seriously impairs its utility for emulsion-making, not only because its power of "setting" is diminished, but also because the products of its decomposition have a tendency to reduce the silver haloid directly, i.e. without exposure to light, and thus to give an emulsion which "fogs" on development. With respect to the various processes for preparing gelatine emulsions I must refer you for practical details to the works devoted to photographic manipulation.[1] I propose to give only a sufficiently concise account to enable you to understand the general method of their preparation, drawing comparisons between gelatine and collodion emulsions whenever we can learn any point of importance from such mode of treatment. The bromide emulsion is the most familiar, although for certain purposes the gelatino-chloride emulsion is preferred. The former will

[1] See for instance Abney's *Photography with Emulsions*, 1885, or Eder's *Ausführliches Handbuch der Photographie*, th. iii., "Die Photographie mit Bromsilber-Gelatine und Chlorsilber-Gelatine," Halle, 1886.

however be sufficiently typical for our present purpose.

In order to prepare an emulsion of a silver haloid with gelatine, we may either mix the silver nitrate solution with the gelatine solution and add the soluble haloid, or we may mix the latter solution with the gelatine and add the silver nitrate. In either case the result is the same—the silver haloid is precipitated in the gelatine solution and is emulsified therein by agitation in just the same manner as it is in making a collodion emulsion. Potassium bromide (sometimes mixed with a little iodide) is the soluble haloid generally employed [B]. There is one point in which gelatino-bromide differs from collodion emulsion which it is essential to bear in mind, and that is that the quantity of potassium bromide is so adjusted as to leave no excess of silver nitrate. It will be instructive to consider the chemical reasons for this difference between the two emulsions.

It is a well-known fact that organic colloidal substances, such as gelatine and albumen, form

decompose these silver compounds. This is the precaution which has to be taken, and I hope the reason is now sufficiently clear. The nitric acid in a collodion emulsion performs a similar function to the excess of potassium bromide in a gelatine emulsion. The acid, after it has done its work, is of course removed by the washing process.

It will be remembered in connection with collodion emulsions that the silver bromide when first precipitated is not in its most sensitive condition, but takes a certain time to reach this state,—the period of ripening. The same property is shown by a gelatino-bromide emulsion and in a much more striking manner. When first precipitated in the emulsion the silver bromide is in an extremely fine state of division, the size of the particles being to a great extent determined by the state of dilution or concentration of the solutions of gelatine and silver nitrate and of the potassium bromide. The size of these finest particles has been determined by Eder from micrometric measurements to be

from ·0008 to ·0015 of a millimeter in diameter. In this stage a gelatino-bromide emulsion offers but little advantage over a collodion emulsion from the point of view of sensitiveness. Now in 1878 it was observed by Bennett that if a gelatine emulsion is allowed to stand for about a week at a moderate temperature (32° C.) the sensitiveness became increased. It was then found by Stuart Wortley that the ripening of the emulsion could be accelerated by increasing the temperature to 60° C., a few hours at this temperature producing the same sensitiveness as many days ripening in the cold. In 1879 Mansfield carried this principle a stage further and showed that by keeping the emulsion at the temperature of boiling water for less than an hour, the maximum of practical sensitiveness could be reached. This is the culminating point in the history of our modern dry-plate processes.

After the precipitation of the silver bromide in the gelatine solution the next step in the preparation of the emulsion is to ripen it, and this

is done by placing the vessel containing the gelatino-bromide in a bath of boiling water and keeping it there with occasional agitation for thirty or forty minutes. The proportions of gelatine and water given in the published formulæ, have been selected by experience as being the best for precipitating the silver bromide in such a state of molecular aggregation as to insure that the ripening takes place in the shortest possible time. The reason of this will appear subsequently.

When the operation of ripening is completed the emulsion is cooled and, if not already of the right consistency, is made up to the proper strength by dilution with a further quantity of gelatine solution. It is obvious that at this stage we have a jelly containing potassium nitrate and excess of potassium bromide in addition to the silver bromide. For reasons which have already been explained in connection with collodion emulsions the soluble and crystallizable salts must be removed before the emulsion film can be allowed to dry on the plates. There is also a

special chemical reason why no excess of potassium bromide should be left in the emulsion, which we shall be in a better position to appreciate later on in this course. The cold emulsion is therefore washed, being first reduced by mechanical means (forcing through the meshes of canvas) to a fine state of division and then treated with cold water till the soluble salts have been dissolved out. The washed emulsion is redissolved in warm water, the solution is filtered, and the plates can then be coated with a uniform film and allowed to dry.

There is one operation in the process of making a gelatine emulsion which possesses a certain fascination—I allude to the ripening of the silver haloid. The gradual change in molecular state is certainly a very remarkable phenomenon, and its investigation, apart from the question of practical utility, cannot but lead to important results in the domain of molecular physics. The researches of investigators who have occupied themselves with this subject, and especially those of Van Monckhoven, Eder, Abney, and Vogel,

tend to show that the change is a purely physical one. The increase in sensitiveness is accompanied by and is probably the result of an actual increase in the size of the particles of silver bromide. The micrometric measurements of Eder have shown that the most sensitive form of emulsion contains particles of from ·003 to ·004 of a millimeter in diameter. If the ripening is continued for too long a period the particles still go on growing, but chemical action at length begins to take place. In other words, if silver bromide be heated for too long a time with the gelatine solution, it becomes reduced and gives rise to products which are directly acted upon by the developer and thus produce fog. This is the reason why it is necessary to precipitate the bromide in the first place in such a state of aggregation as to insure the maximum degree of ripeness with the minimum amount of heating.

Not only is the ripening accompanied by an increase in the size of the bromide particles, but the molecular growth is associated with changes in the optical properties which enable

the operator to ascertain whether the emulsion is of the proper degree of sensitiveness. The first precipitated bromide is yellowish white by reflected light and reddish by transmitted light; this is the insensitive, unripened condition. As the particles grow the light transmitted by a layer of the emulsion becomes richer in blue and violet and poorer in red rays. In other words, the larger particles absorb more of the red rays and allow more of the blue and violet rays to pass through. When ripe the emulsion is grey or greyish violet by transmitted light, and the silver bromide appears greenish by reflected light. This is the most sensitive form of the haloid, and is the condition sought in the preparation of the emulsion.

The changes undergone by the silver bromide are, as I have already stated, of a physical character and are not accompanied by any change in chemical composition. If the gelatine is dissolved out of a ripened emulsion the residual bromide has the normal composition corresponding to the formula AgBr. Moreover, the emulsion,

if well prepared, is not acted upon by the developer unless previously exposed to light, even when the extreme of sensitiveness is attained. It is therefore evident that the bromide in the most sensitive emulsion is not present in the same chemical condition as it is after photo-decomposition. But we know that over ripening causes a decomposition of the bromide and enables it to be acted upon directly by the developer without previous exposure—in other words prolonged heating of the silver haloid in the presence of gelatine produces a similar effect to a short exposure to light. In an over-ripened emulsion we have overstepped the boundary of physical change and have entered the region of chemical change. This molecular transformation of the silver salt from a small-particled, insensitive state to a larger-particled, sensitive condition, thus introduces a new factor into the question of the photo-instability of a chemical compound. The physical state of aggregation must be taken into consideration as well as those other chemical conditions which have been shown to have a

determining influence upon the sensitiveness of photo-decomposable compounds.

The fact that the chloride and bromide of silver are capable of existing in different molecular states has long been known, detailed accounts of the various modifications having been published by Stas in 1874. This eminent investigator even observed that by the prolonged boiling of silver bromide with water, the salt acquired an increased sensitiveness analogous to that which takes place in the process of ripening. With respect to the growth in size of the silver bromide particles during this last process some further explanation will be necessary, and this is the most favourable opportunity for considering the subject.

Silver bromide is practically insoluble in water, but the presence of potassium bromide and gelatine in hot aqueous solution enables a perceptible quantity of the silver salt to be dissolved up. Let me illustrate this by reversing an experiment shown in an earlier part of the present lecture. If we take a solution of potassium bromide and gelatine in water and add silver

nitrate solution, we must put in more of the latter to produce a precipitate when gelatine is present than when the same amount of potassium bromide is dissolved in the same quantity of water without the addition of gelatine [E]. In other words silver bromide is perceptibly soluble in excess of potassium bromide and especially in the presence of gelatine. Now in the emulsion undergoing ripening we have a hot solution of gelatine containing potassium bromide —the conditions most favourable for dissolving up some of the silver bromide. There are reasons for believing that the growth of the particles is due to this solvent action of the menstruum, which is always saturated with dissolved silver bromide, and which continually deposits this salt on the particles of the bromide already present, thus causing the increase in the size of the latter. For this reason it is indispensable that an excess of potassium bromide should be present in a gelatine emulsion which is to be ripened by heat.

There is yet another method of ripening a gelatine emulsion to which attention must be

called before we can leave emulsion photography. It has been found that ammonia acts in the same way as heat in causing the silver bromide to acquire its sensitive condition. There are different ways of working this process, and there are numerous formulæ into the details of which I cannot now enter but for which I must refer you to the practical treatises. As a point of history it should be mentioned that the ammonia process of ripening has been developed chiefly by Van Monckhoven and by Eder and Pizzighelli. With respect to manipulation it will suffice to state that in the preparation of such an emulsion, we may add an ammoniacal solution of silver nitrate to a solution of potassium bromide in aqueous gelatine and ripen the mixture at a gentle heat; or the emulsion may be first partially ripened in the usual way, and then the sensitiveness of the silver haloid brought up to the desired stage by the addition of ammonia, and continuing the digestion for a short time at a lower temperature. The ripening faculty possessed by ammonia has been successfully applied in cold

emulsifying processes, such as those of Cowan and Henderson.

We must pause here and ask ourselves why it is that ammonia acts as a ripening agent. The immediate cause is doubtless the solubility of silver bromide in ammonia, a property familiar to all who are acquainted with the characters of the silver haloids. On diluting the ammoniacal solution with water, or on driving off the ammonia by heat, the dissolved bromide is reprecipitated [F]. An action of this kind no doubt goes on during the ammonia ripening process, the growth of the bromide particles taking place by the gradual deposition of bromide from the solution on to the particles already in suspension, just in the same manner as in the alternative method of ripening by digestion. That the increase of sensitiveness is due to a physical and not to a chemical change, may be proved by arguments similar to those which have been made use of in dealing with the alternative process of ripening, and there is no occasion to repeat them here.

I have dealt at some length with the ripening

process, but it must not be concluded that the extreme sensitiveness of a gelatine emulsion is due solely to the molecular state of the silver haloid. There are other conditions which have to be taken into consideration before we can take leave of this part of the subject. You will remember that in a washed collodion emulsion we are at the mercy of the preservative for sensitizing action. Now in a gelatine emulsion the vehicle itself is a bromine absorbent—*the gelatine is also a sensitizer*, and because of the intimate contact which everywhere exists between the gelatine and the imbedded silver haloid particles, the sensitizing action is capable of being exerted in the most perfect conceivable manner short of the vehicle being actually in a state of solution. Then again, the perfect imbedding of the silver haloid particles in the gelatine enables us to use developers of great strength, and thus to make the most out of the impression produced on exposure; but this part of the subject will be better understood after we have dealt with the theory of development. The co-operation of all these condi-

tions, both physical and chemical, has resulted in the production of a mixture which, for sensitiveness towards light, transcends anything that has hitherto been discovered, and has placed in the hands of modern photographers a series of methods which, for rapidity and convenience of manipulation, must surpass the wildest hopes ever entertained by the early pioneers of the art.

The practical applications of gelatine emulsions to photographic purposes are sufficiently well known and need not be dealt with at length in the present course of lectures. The extreme sensitiveness of such films enables us to secure instantaneous impressions of moving objects such as breaking waves, yachts at sea, express trains, animals in motion or birds in flight, and all the other wonderful effects with which we have been familiarized of late years. The problems connected with the locomotion of animals and the flight of birds have been recently considerably advanced towards solution by the use of cameras with revolving slides, capable of taking many

pictures in the course of a second of time.[1] The easy manipulation of the emulsion enables it to be spread uniformly over the surface of paper, so that the operator can take into the field a very large amount of sensitive surface having but little weight and occupying but a small space—such an area of sensitive film as would have been impossible in the days of glass plate negatives. One of the latest developments in this direction enables the photographer to take no less than four dozen negatives on one continuous roll of sensitized paper.[2] These pictures can be developed at any convenient time after exposure, and the film with its developed image stripped off and transferred to a thin transparent sheet of gelatine so as to form a light negative which is practically unbreakable, and from which any number of prints can be obtained in the usual way.

In its application to other branches of science modern photography has already proved to be of

[1] See *Nature*, February 16, 1888.

[2] Reference is here made to the Eastman Stripping Film. By the courtesy of the Company a demonstration of the process was given at the termination of the lecture.

the very highest value, and holds out still greater prospects for the future.[1] This particularly applies to astronomy, in which science the sensitive emulsion bids fair to largely supersede the older and more wearisome methods of eye observation. Almost from the dawn of its discovery by Daguerre, attempts were made to utilize photography for securing pictures of the heavenly bodies. The collodion wet plate was first successfully applied by De la Rue in 1852 to the production of lunar photographs, and through the kindness of Mr. Joseph Beck I am enabled to show you on the screen some of Mr. De la Rue's original pictures. Lunar photography was afterwards brought to a considerable degree of perfection in America by Mr. L. M. Rutherfurd and the late Dr. Henry Draper. The mapping of the moon's surface by the aid of gelatine dry plates is now being carried on at Paris by the brothers Henry.

[1] One of the latest applications of highly sensitive plates is by Professor Oettingen, of Dorpat, who has secured impressions of the flash produced by the combustion of hydrogen and oxygen in a closed vessel showing the intermittent character of the explosion.

With respect to solar photography the difficulty is one of brightness; owing to the excessive brilliancy of the sun, special flashing shutters have to be employed in order to avoid over exposure. The sun's disc is however capable of being photographically registered with all its rapidly changing details of structure with an exposure according to M. Janssen, our most successful worker in this branch, of $\frac{1}{100000}$ of a second. The splendid sun pictures produced at Meudon by this last observer have been familiar to astronomers for the last ten years. The camera was first successfully applied to the registration of a total solar eclipse by De la Rue and Secchi in 1860, and no eclipse has since taken place in which the aid of photography has not been called into requisition. Whenever visible the sun is made to give a daily impression of himself on photographic plates in several observatories both here and abroad, so that the appearance and position of the spots which are so frequently seen on his surface are automatically recorded. By the courtesy of the Astronomer-Royal I have here for your inspection

some specimens of the Greenwich sun photographs.

It is evident that the wet collodion process presents many disadvantages for astronomical work. Among its drawbacks I need only mention the necessity for coating and sensitizing each plate immediately before use, and the limited time of exposure admitted by such a moist film. For this last reason the process is not at all adapted for the photography of faint objects, such as stars and nebulæ, which require prolonged exposure. This difficulty is of course overcome by the use of gelatine emulsion plates which can if necessary be exposed for hours. By means of highly sensitive dry plates the stars can now be photographed in their myriads—it is only a question of mechanical perfection of adjustment in the driving gear which compensates for the earth's rotation, and length of exposure. Distant suns and nebulæ too faint to be seen by human eye with the best of instruments, and so remote that their light may take years to reach the earth, can be made to record themselves faithfully on that

surface which has been well described as "the retina which never forgets."

The first successful use of gelatine emulsion for astronomical photography was made by Dr. Huggins, who, in 1876, secured impressions of stellar spectra on dry plates. The work has been followed up in all countries by observers too numerous to mention. One of our most successful workers, Mr. A. A. Common, whose magnificent photograph of the great nebula in Orion taken in 1883 is so well known to astronomers, has been good enough to forward some specimens of his achievements for exhibition. The success which has attended the use of gelatine dry plates resulted last year (1886) in the meeting of an International Congress in Paris at the instigation of Mr. David Gill, Her Majesty's Astronomer at the Cape, for the purpose of discussing a scheme for a joint astro-photographic survey. All the stars in the heaven down to the fourteenth magnitude[1] are to be photographed by the different nations

[1] The best results obtained by Rutherfurd with wet collodion plates in 1864 showed stars down to the ninth magnitude.

taking part in the work. A series of about 10,000 photographs will by this means be secured in the course of five years on which will be recorded some twenty million stars—material for a celestial chart which, when completed, will be a tribute to the utility of modern photographic methods such as has never before been paid by one branch of science to another.

APPENDIX TO LECTURE IV.

A (p. 107).—The principle of emulsification can be illustrated by the following experiment:—Two flasks, each containing about 100 c.c., are filled up to the same level, one with a 6 per cent. solution of zinc bromide in water, and the other with collodion salted with the same quantity of zinc bromide. It is more satisfactory to weigh out the materials and make the solutions in the lecture room. A quantity of silver nitrate equivalent to the whole quantity of zinc bromide in the two flasks is then dissolved in alcohol with a little water, and the solution divided into two equal parts, one of which is added to the aqueous zinc bromide solution, and the other to the salted collodion. The same amount of silver bromide is of course formed in each flask, and on briskly agitating, the bromide formed in the aqueous solution soon becomes granular and settles to the bottom on standing, while that formed in the collodion emulsifies.

B (p. 117).—The emulsification of silver bromide in gelatine is easily shown by the following experiment:—Soak 20 grams of gelatine in a little water for half an hour and then dissolve completely, by the aid of heat, in a larger quantity of water and add 12 grams of potassium bromide to the solution, which should be made up to 150 c.c. This bromized gelatine solution, when cool has poured into it gradually with occasional agitation a solution of 15 grams silver nitrate in 150 c.c. water. The operation is best conducted in a glass flask, the two solutions being prepared before the lecture. It makes the experiment more instructive if a companion flask is prepared with a solution of 12 grams of potassium bromide in 150 c.c. water, and a solution of 15 grams silver nitrate in 150 c.c. water is gradually poured into this with brisk agitation. The silver bromide precipitated in the latter case becomes granular and soon subsides, while that precipitated in the gelatine solution emulsifies.

C (p. 118).—Into two beakers or flasks introduce the same bulk of (1) distilled water, and (2) a 2 per cent. solution of gelatine. Add to each flask the same quantity of silver nitrate solution, only a very small quantity of this salt being necessary—just enough to give a *distinct* precipitate when potassium bromide is added to the aqueous solution.

From a burette allow a weak solution (exact strength immaterial) of potassium bromide to run into each flask. It will be found that (1) gives an immediate turbidity, while (2) will require much more of the bromide solution before a precipitate forms.

D (p. 118).—Some inferior gelatine is dissolved in water and a few drops of silver nitrate solution added. The flask is heated in a water bath till the solution begins to darken. This experiment serves to show the reducing action of the gelatine upon the silver salt.

E (p. 128).—A strong solution of potassium bromide (about 20 per cent.) is divided into two equal portions, to one of which is added about one-fourth its volume of a 5 per cent. solution of gelatine, and to the other the same quantity of water. The two solutions of course contain the same quantity of potassium bromide per c.c. A weak solution of silver nitrate is now run into each beaker (from a burette). It will be found that the solution containing the gelatine requires a much larger quantity of silver nitrate to produce a precipitate than the purely aqueous solution.

F (p. 130).—A clear ammoniacal solution of silver bromide is divided into two portions, one of which is boiled and the other diluted with water. In both cases the dissolved bromide is precipitated.

LECTURE V.

General Notions of Development.—The Latent or Invisible Image.—The Action of Sensitizers in Different Processes.—Theory of Developers and Restrainers.—Development by Vapours.—Acid Development by Ferrous Sulphate.—Alkaline Development by Ammonium Pyrogallate and by Ferrous Oxalate.

THE processes which have now been considered may be regarded as so many ways of obtaining a film of silver haloid of more or less sensitiveness on which the picture formed by a lens can be made to impress itself in an invisible form on exposure for a suitable period. In order to make this invisible or latent image reveal itself you all know that certain substances called "developers" have to be applied to the film, and this process of development must next engage our attention.

There is even now in this age of startling scientific effects hardly any phenomenon more striking than the gradual appearance of a picture, with all its delicate gradations of light and shade, on what was apparently a homogeneous surface, on the application of the developing solution.

In general terms a developing agent may be described as a substance which exerts an action upon those portions of a photo-sensitive compound which have been exposed to light different to that which it exerts upon the unexposed portions. If this difference of action is associated with a difference in colour, while the colour of the photo-reduction product does not differ to any striking extent from that of the unreduced compound, we may have a strong contrast brought out on development. This point is well illustrated by the experiments shown in the first lecture with ferric and uranic salts. It will be remembered that a ferric salt becomes reduced to the ferrous state on exposure, but since the latter does not differ very strikingly in colour from the ferric salt, a ferrous design on a ferric background is hardly perceptible

at a distance. The same remark applies to a uranous design on a uranic background. On washing the exposed surfaces with a solution of potassium ferricyanide you know what happens. The ferrous design becomes developed in blue and the uranous design in brown, owing to the formation of the corresponding ferricyanides. The colour of the design is in these cases an accident contingent upon the fact that ferrous ferricyanide is blue and the uranous ferricyanide brown. By using another developer we may impart a different colour to the design. The salts of gold and silver for example, are reduced by uranous compounds but not by uranic compounds, so that if we wash the surface of the exposed uranium print with gold chloride solution, the uranous design only is acted upon and is "developed" in finely divided reduced gold which produces a picture of a purple colour. Similarly if we use a solution of silver nitrate the uranous design is developed in grey, owing to the deposition of metallic silver reduced from the nitrate by the uranous compound [A]. The chemistry of such processes of development as

these is comparatively simple, and may be represented by the well-known reduction of gold and silver salts by ferrous salts:—

$$6FeSO_4 + 6AgNO_3 = 2Fe_2(SO_4)_3 + Fe_2(NO_3)_6 + 3Ag_2$$
$$3Fe_2Cl_4 + 2AuCl_3 = 3Fe_2Cl_6 + Au_2$$

There is another point brought out by the examples chosen to illustrate the general principle of photographic development which may advantageously be dealt with now. Not only is the colour of the developed image dependent on the nature of the developer, but the production of a positive or negative is also in a sense accidental. Thus supposing a pattern to be cut out in a sheet of black paper and a ferric coated surface exposed under the latter, the ferrous design thus impressed might be regarded as a negative because it appears lighter than the background of unaltered ferric compound. But on washing with ferricyanide the faint negative image becomes converted into a blue ositive, because it happens that the colour given y the photo-reduction product with the ferricyan-

ide is much more intense than the ground colour. Now if instead of using a ferricyanide we use as a developer some salt which gives a darker colour with the ferric than with the ferrous compound, such for instance as a ferrocyanide, matters are reversed, and we get a negative instead of a positive on development [B].

From these preliminary considerations you will be enabled to gain a general idea of the function of a developer, and at the same time the ground will have been cleared by the establishment of the principle that the developed image may be positive or negative according to the nature of the photo-reduction product on the one hand and of the developer on the other hand. We must consider development in the abstract, and so far as we are at present concerned, the fact of a picture being positive or negative in any particular case must be regarded as accidental to the process with which we are dealing.

The next point that claims attention is the nature of that invisible image which is formed on the sensitive film, and which is revealed by the process

of development. As long as we had to do with compounds which underwent a visible change in colour under the influence of light, no such mystery as that involved in the formation of an invisible picture obtruded itself upon our notice: as long as we were in the region of photo-chemistry proper, we had only to regard the change in colour as due to the production of some coloured product of reduction. But as soon as we came to consider the photographic processes themselves, this apparently new kind of photo-chemical action presented itself. In discussing this subject it will be necessary to limit ourselves to those compounds universally employed for photographic purposes, viz. the silver haloids. What is the nature of the image which exists on the surface of a sensitive film after exposure in the camera? has this image any relationship to the visible product of reduction resulting from the action of light upon the silver haloids in the presence of sensitizers?

In answer to these questions it is now generally dmitted that the invisible image is of the same hemical composition as the darkened products of

photo-decomposition—that it differs from the latter only in degree and not in kind. There are many good reasons for this belief, although these are necessarily of an indirect kind. The difficulties of investigating this subject are evidently great, owing to the extremely minute amount of the silver haloid which undergoes photo-decomposition on the surface of what is in itself nothing more than a film. If the investigation of the photo-reduction products of the silver haloids exposed in large quantities to the action of light has hitherto baffled ingenuity, you will readily understand that the direct demonstration of the composition of the latent image is at present utterly beyond the reach of our most refined chemical methods. The reasons which have led to the belief that this invisible image is built up of the same material as the darkened haloid are that the substances which accelerate or retard the formation of the latter act in a precisely similar manner with respect to the latent picture. A substance like silver nitrate which, as we have seen, so greatly facilitates the decomposition of the haloid acts also

as a sensitizer in all photographic processes: substances like mercuric, stannic or ferric salts, which are inimical to the liberation of free halogen, enormously diminish the sensitiveness of the photographic film [C].

This kind of evidence—and there is much more of a similar nature if I only had time to submit it to you—enables us to bridge over the gap between photo-chemistry and photographic chemistry. We may regard the invisible image as being formed of an oxyhaloid salt of silver or of a combination of such a salt with unaltered haloid (photosalt). The fate of the infinitesimal quantity of liberated halogen will depend entirely upon the nature of the sensitizer, but it is evident that in order to get the maximum sensitiveness of a photographic surface—that is, to get an invisible image formed with the minimum of exposure, we must have some halogen absorbent present, a necessity first distinctly formulated by Prof. H. W. Vogel of Berlin. It will be instructive to consider the action of the sensitizer in the more important photographic processes.

In the Daguerreotype plate a film of silver iodide is supported on a substratum of silver, and it is difficult at first sight to imagine what the sensitizer can be. It is generally supposed that the silver itself plays this part by absorbing the liberated iodine, and this is proved by an experiment made known in 1866 by Poitevin. A film of collodion containing silver iodide perfectly free from excess of silver nitrate, was pressed on to the surface of a silver plate and exposed to light. The plate thus coated was found to be far more sensitive than a glass plate coated with the same collodion, clearly showing that the metallic silver acted as a sensitizer. But the sensitizing action in this case is not entirely due to the silver, because a film of pure silver iodide on glass, prepared by iodizing a silver mirror deposited on glass, also gives a latent developable image on exposure. The action is certainly very feeble under these conditions, and a long exposure in strong light is required to produce much effect, but the result is important because it shows that silver iodide can act to some extent as its own

sensitizer. This property of silver iodide might have been anticipated from the analogy which is well known to exist between silver and the metals of the alkalies. Potassium for example forms the tri-iodide KI_3, and the existence of this compound prepares us for the belief that silver iodide may be capable of combining with a further quantity of iodine.

In a former lecture I stated that the Daguerreotype plate had much to teach us, and we can now extract a little further information from the facts which have just been considered. These facts emphasize very clearly the principle previously laid down—that the sensitiveness of any system is a function both of the photo-instability of the compound and of the affinity of the sensitizer for one of the constituents of the compound. Consider the sensitiveness of a Daguerreotype plate as compared with that of a film of pure silver iodide on glass. In the first case we have the system AgI+Ag, and in the second case the system AgI+AgI, *i.e.* the relatively strong affinity of metallic silver for the liberated iodine as com-

pared with the feeble affinity of silver iodide for iodine, this difference in sensitizing efficiency determining the superior sensitiveness of the first system.

In the Talbotype process the sensitizer is, as you know, silver nitrate in conjunction with gallic acid, and in the wet collodion process silver nitrate alone. The sensitizing action of this last salt is due to the readiness with which it absorbs the liberated halogen. In the case of iodine, for instance, the reaction is usually represented by the following equation :—

$$3I_2 + 6AgNO_3 + 3H_2O = 5AgI + AgIO_3 + 6HNO_3.$$

The products according to this scheme would be silver iodide and iodate and nitric acid, the free iodine of course resulting from the photo-decomposition of silver iodide.[1]

In the dry plate and emulsion processes either

[1] This requires corroboration. It is known that silver chloride when exposed to light in the presence of silver nitrate gives a strongly acid solution, but the amount of free nitric acid formed has not yet been determined.

the preservative, as in the case of tannin, or the vehicle itself, as in the case of gelatine, is the sensitizer. The precise nature of the products formed when these organic sensitizers are acted upon by the liberated halogens is unknown, but this is immaterial from our present point of view. As a practical detail I may mention that gelatine will absorb over 20 per cent of its weight of bromine from bromine water in four days at ordinary atmospheric temperatures, the product consisting of brominated compounds of unknown constitution.

So much for the chemical action of sensitizers—now let us return to the consideration of the invisible image armed with this knowledge of the conditions essential to its formation. That the image formed by the short exposure of a sensitive film of silver haloid should be invisible may at first appear surprising, but the wonder will vanish if we just call to mind how infinitesimal in quantity is the reduction product formed. The action is purely superficial—the surface layer of reduced haloid must be of such extreme thinness as to

present in transverse section a diameter comparable with the actual size of the molecules themselves. Nor must it be forgotten that the reduction product, except in the case of the chloride, is by no means highly coloured. For these reasons it can hardly be expected that the undeveloped picture should be anything but invisible.

We must therefore regard the image formed by the camera lens as being painted in reduction product on the surface of the sensitive film, the varying intensity of action corresponding to the lights and shades being represented by varying amount of reduction product. In the strongest lights we have the maximum amount of decomposition—the greatest number of silver haloid molecules are there decomposed, while in the feebler lights fewer molecules are decomposed, and in the deep shadows there is no decomposition at all. The actual state of affairs can be represented diagrammatically by taking a simple case. Imagine three squares of paper on an orange, "non-actinic wall," one square (A) being black,

the other (C) white, and the third (B) of an intermediate shade :—

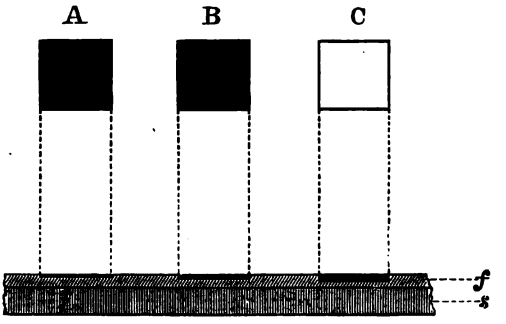


FIG. 3.

f, film; *s*, substratum. A, B, and C are seen in elevation; *f* and *s* in section.

If these squares were photographed the black would produce the smallest amount of decomposition, the white the largest amount of decomposition, and the intermediate shade an intermediate amount of decomposition. The quantity of reduction product formed by each square is shown in the section of the film, of course on an exaggerated scale.[1]

[1] The amount of silver haloid decomposed is strictly speaking not directly proportional to the intensity of the light in all cases. The relative amount varies in different films, but this consideration

Such being the state of affairs on the surface of the film to which the developer is applied, we may now proceed to consider the methods of development, selecting for this purpose types of developers which have been or are in actual use by photographers. Commencing with the Daguerreotype the latent picture is, as you are aware, developed in this process by exposure to mercury vapour. This mode of development stands alone as a type of the action of vapours upon the invisible image. It is stated that the process was discovered accidentally by Daguerre, who put one of his exposed plates with nothing visible on it away in a cupboard, and the next morning found a picture developed, this result being ultimately traced to a vessel of mercury on one of the shelves.

In a case of this kind development is evidently due to the circumstance that mercury vapour can form a compound with the product of reduction and not with the unaltered haloid. The

may be neglected in a coarse illustration such as that made use of above.

amount of mercury deposited is proportional to the amount of reduction product formed on different parts of the plate, and in this way the picture is built up. It is sometimes asserted that the reduction product *attracts* the mercury vapour, but this hardly expresses the facts of the case. We must consider the plate over a vessel of warm mercury as being subjected to a constant bombardment of mercury molecules over the whole surface. Where the molecules meet reduction product there they remain attached—where they meet unaltered haloid they fly off again, so that the reduction product alone ultimately retains a layer of molecules of varying thickness. The action might be roughly represented by taking a sheet of glass on which a design had been painted in gum, and blowing sand on to the surface. Where the sand met glass it would fall off, where it met gum it would be retained, and the design would be thus "developed" in sand particles [D]. As far as the physical action is concerned this explanation must at present suffice, but the chemical nature of the compound formed

by mercury with the reduction product is at present unknown. It is not even known whether any definite compound is formed at all; it is possible that the action is purely physical, the reduction product being capable of being "wetted," so to speak, by the condensed mercury, while the unaltered haloid is not. In this connection it may be mentioned that the Daguerreotype picture is capable of being developed by water vapour, although of course only in a transitory way. I may be excused for once again emphasizing how much we have yet to learn from this oldest known photographic process with respect both to its physical and chemical principles.

The iron developer so generally employed in the wet collodion process will serve as a type of the next class of developers. The solution contains as essentials ferrous sulphate and acetic acid, some alcohol being added to insure the uniform flow of the solution over the surface of the plate. Let us first consider the action of this developer from a chemical point of view. Ferrous salts—which were first used in photo-

graphy by Robert Hunt in 1844—are reducing agents which readily reduce silver nitrate, but have practically no reducing action on the silver haloids under ordinary conditions. If we add ferrous sulphate to a solution of silver nitrate we get a precipitate of metallic silver [E], formed in accordance with the reaction referred to a short time ago :—

$$6FeSO_4 + 6AgNO_3 = 2Fe_2(SO_4)_3 + Fe_2(NO_3)_6 + 3Ag_2$$

Now the collodion plate with its invisible image is covered with the sensitizing film of silver nitrate, and if we poured on to this a solution of ferrous sulphate, we should of course have a film of reduced silver immediately deposited all over the plate. The acetic acid prevents this disaster by checking the reduction of the silver nitrate, so that the free silver is gradually deposited on the reduction product, the amount of deposit being, broadly speaking, proportional to the amount of this product. In this way the picture is built up in metallic silver.

This explanation of the action of the iron developer is of course a mere outline sketch, some of the details of which I must now endeavour to supply. Let us first consider what can be learnt from the use of acetic acid, which retards the precipitation of silver from the solutions of its salts by the action of reducing agents, although the metal itself is insoluble in the acid. Substances which exert this retarding action are called *restrainers*, and these act with more or less completeness according to the stability of the compound which they form with silver. If the restrainer forms a very stable silver compound we may have any degree of retardation up to the total prevention of the precipitation of silver. The organic salts of silver are less stable than the inorganic salts, and the organic acids are accordingly milder restrainers than the mineral acids. Even indifferent organic substances, such as sugar, glycerol, or gelatine, act as restrainers by virtue of the viscosity which they confer upon the developing solution, or because of a tendency to form feeble compounds with the "nascent"

silver. Such substances are sometimes spoken of as "physical restrainers" in order to distinguish them from acids or compounds which are capable of combining chemically with the silver, and which may therefore be regarded as chemical restrainers [F].

The next point to be considered is one of considerable importance — it lies at the root of the explanation of the development of the invisible image in silver. Why is it that the nascent silver attaches itself only to the reduction product? Important as is this question to the theory of photographic development, it cannot be satisfactorily answered in the present state of knowledge. It is generally stated that the reduced haloid, *i.e.*, the invisible image, ***attracts*** the nascent silver from the developing solution. But this statement must be carried further before the theory of the developer can be considered in any way complete. It is obvious that the reduction product attracts the silver, otherwise the picture would not be developed at all To say therefore that the silver is attracted does not carry the explanation very far — it amounts in

reality to little more than a restatement of the fact. All who have used the iron developer know that like all other developers it is cumulative in its action; the picture gradually gains in intensity by the accumulation of fresh silver on the deposit first formed. Now the question is, does the deposit of reduced silver begin to form at once upon the reduction product, or is the latter in the first place superficially reduced to the metallic state by the developer? In other words, can the reduction product be reduced further by ferrous sulphate?

These are the questions which it is now very difficult to answer, and I am glad of the present opportunity of pointing out a line of investigation which might easily be taken up by any one of you who has the requisite chemical knowledge. It is generally believed that no direct reduction of the invisible image by the ferrous sulphate takes place in this kind of development,[1] but that the nascent silver is from the very beginning of the process deposited on the reduction product only. What-

[1] Some experiments made for me by Mr. T. H. Norris in the laboratory of the Finsbury Technical College confirm this belief.

ever may be the truth with respect to the initial action, there is no doubt that the silver deposit when once formed continues to grow as long as there is any silver to feed it. This mode of deposition will remind you of electrolytic action or of crystalline growth. Evidence is not wanting that the growth of the silver deposit may be a case of electro-deposition, the film of silver first formed constituting one element of a micro-galvanic couple excited by the developing solution. It has been shown by Lermontoff that with solutions of silver nitrate and ferrous sulphate and a strip of metallic silver a galvanic circuit can be formed, the nitrate becoming reduced and depositing a crystalline growth of metallic silver on the silver strip [G].

The development of the photographic image by means of the ferrous sulphate developer thus resolves itself ultimately into a process of accretion. Given a faint silver picture to start with, and the metallic deposit will go on gaining in thickness as ' ng as there is nascent silver to feed it. We can iitate these conditions artificially without calling the aid of light at all. Here for instance is a

sheet of paper coated with silver chloride on which stripes of metallic silver have been produced by reduction. The stripes are at present faint, but on brushing them over with a solution of ferrous sulphate containing acetic acid and a little silver nitrate, they become almost black, owing to the further deposition of silver upon them [H]. The conditions in this experiment are much about the same as in an ordinary photographic plate undergoing development. We have a surface composed partly of unaltered haloid and partly of metallic silver, the nascent silver from the developer being deposited on the metallic stripes only and none on the unreduced haloid.

It will be readily gathered from these explanations that the developers typified by the iron developer build up a visible picture by depositing reduced silver on the invisible image. That the reduced silver is supplied by the nitrate and not by the haloid is easily shown by exposing a wet collodion plate and then washing out the excess of silver nitrate before applying the developer. Under these circumstances no picture is developed at all

or at most only a very faint one, probably the result of the retained trace of silver nitrate which is so difficult to remove by washing. On adding a few drops of silver nitrate to the developer such a washed plate can be developed as usual [I]. Any mixture of substances containing what may be called a potential silver deposit will act as a developer when the requisite conditions, electro-chemical or otherwise, are set up. All that is necessary is a reducing agent capable of reducing silver nitrate and not the unaltered haloid, and capable of having its reducing power modified if requisite by a restrainer. It is quite unnecessary here in dealing only with general principles to specify all the different kinds of developers which act in the way indicated. As illustrating the general theory an experiment of Carey Lea's is highly instructive. An iodized collodion wet plate after exposure is washed free from silver nitrate, and is then treated with a solution of mercurous nitrate and pyrogallol when the invisible image is developed in mercury. The analogy of this developer with the iron developer is sufficiently

obvious — the solution contains a potential deposit of mercury, and the image is accordingly developed in this metal instead of in silver.

Another important group of developers may be typified by the alkaline developer so familiar to all who have worked with gelatine emulsion plates. A word or two as to the history of this kind of development may not be out of place. Gallic acid, which was first obtained pure by Scheele in 1786, was used as a developer in the early days of the Talbotype process. The crystalline sublimate obtained by heating gallic acid was first identified as a distinct substance (pyrogallic acid) by Braconnot in 1831, and its use as a photographic developer was suggested in 1851 by Liebig and Regnault. It was the late Colonel Russell who, as I stated in a former lecture, first made known in 1862 the advantages of an ammoniacal solution of pyrogallol for the development of dry tannin plates, so that when gelatine emulsion plates came into use there was a developer for them already to hand.

In considering the principles of alkaline develop-

ment the first thing to be borne in mind is that we have no free silver nitrate on the plate as in the collodion process. That is one reason why the ordinary iron developer cannot be used with dry plates. Pyrogallol is, as most of you know, a trihydroxybenzene derived from gallic acid by destructive distillation, carbon dioxide being given off as one of the products of decomposition :—

$$\underset{\text{Gallic acid.}}{C_6H_2(HO)_3.COOH} = \underset{\text{Pyrogallol.}}{C_6H_3(HO)_3} + CO_2$$

An alkaline solution of pyrogallol is a most powerful reducing agent, greedily absorbing oxygen from the air, and rapidly reducing the salts of silver. Not only is silver nitrate reduced by such a solution, but even the silver haloids are reduced, so that we have to deal with a substance of which the reducing power transcends that of ferrous sulphate [J]. For this reason the alkaline pyrogallate cannot be used alone—it requires restraining, or we should have reduction over the whole plate ; in other words, a fog. It has been found that a soluble bromide, such as that of potassium, exerts the necessary restrain-

ing influence, so that the developer actually used consists of an ammoniacal solution of pyrogallol mixed with potassium bromide. The action of the restrainer can be illustrated by an experiment. Here is a sheet of paper coated with silver bromide, and if we paint on its surface a stripe of ammoniacal pyrogallol we get a dark stripe of reduced silver. Now on adding some potassium bromide to the developer and again painting a stripe you see we get a much fainter impression—the reducing action of the bromide has been weakened by the restrainer [K].

So much for the facts—now let us consider their interpretation. The point that chiefly concerns us is the retarding action of the potassium bromide. It is generally believed that the restraining power of this substance is due to its tendency to form a double salt with silver bromide, this double salt being more stable, *i.e.* less easily reducible than the silver bromide itself. That such a double silver potassium bromide exists is rendered probable by the well-known fact of the solubility of silver bromide in a solution of potassium bromide [L].

The restrainer in the alkaline developer acts therefore in a different way to the acetic acid of the iron developer, although the final result is the same. The potassium bromide mixed with the alkaline pyrogallate checks the reduction of the unaltered silver haloid on the plate, and thus prevents the deposition of a film of reduced silver all over the latter. The iron developer, on the other hand, has no tendency to reduce the unaltered haloid, but only the small quantity of silver nitrate which is present on the plate, and the too rapid reduction of this nitrate is checked by the acetic acid, which thus prevents the deposition of a film of silver on the unaltered haloid. The principles of action of the alkaline developer will now be sufficiently clear to enable us to follow the course of the process of development somewhat more deeply.

Supposing we begin with an exposed gelatino-bromide plate; the invisible image is formed of a product which is more easily reducible than the unchanged haloid, so that the first action of the

developer is to reduce the reduction product, *i.e.* the invisible picture, to the metallic state. Now the alkaline developer differs from the iron developer in having no potential deposit of silver dissolved in it. I say *no* potential deposit, but it would be more correct to say that it contains only a trace of dissolved silver, because the ammoniacal pyrogallate does dissolve a trace of silver haloid out of the film, and this becomes reduced and adds to the density of the image. It might appear therefore at first sight that the alkaline developer simply acts by reducing the invisible image to the metallic state, the intensity of the picture being increased by the minute amount of silver resulting from the reduction of the silver bromide dissolved by the ammoniacal developing solution. This explanation however, simple as it may appear, will be found inadequate on further examination. In the first place, it is evident that the amount of reduction product which forms the invisible image is so small that its equivalent in metallic silver would give but the faintest of pictures. In the next place, it can easily be shown

that the amount of silver bromide dissolved out of the film by the ammoniacal solution is nothing more than a trace, and is quite insufficient to account for the density of the fully-developed picture. If a solution of ammonia of about the same strength as that used in the alkaline developer be poured repeatedly over the surface of an unexposed gelatino-bromide plate, it will be found that the merest trace of silver bromide is present in the solution. The density of the deposit in the completely developed picture clearly shows therefore that the metallic image is fed from some other source. Whence comes this additional supply of silver?

The answer to this last question must now be dealt with before the theory of alkaline development can be considered in any way complete. The metallic image produced by the first action of the developer, which image is in fact the equivalent in silver of the reduction product formed by the action of light, comes into existence in the presence of the unaltered bromide in which it is imbedded. We have therefore what may be regarded as nascent

silver in contact with silver bromide, the two kinds of particles being wetted by the developing solution. Under these circumstances the unaltered silver bromide becomes reduced in those places where it is in contact with the nascent silver. It is by this means that the additional silver is supplied which reinforces the film first produced, and gives density to the image. In the case of alkaline development the picture is built up from silver supplied chiefly from the unchanged silver haloid in the emulsion itself—not from the bromide generally, but only from those portions which are in immediate contact with the silver image resulting from the first action of the developer. Thus the image, instead of being built up by accretion from above as in acid development, is supplied by growth from below. In one case the silver picture is raised in relief upon the surface of the collodion; in the other case the image is sunk into the gelatine film. The black, white, and intermediate squares of paper used to illustrate the formation of the latent image (see p. 155) would give, when photographed and developed by the two methods,

results which might be thus represented diagrammatically :—

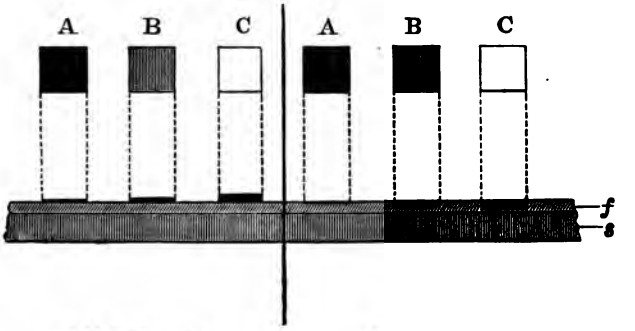


FIG. 4.

In proof of this it is found that if after development the silver image is dissolved off the plate by nitric acid, the surface of the film developed by ferrous sulphate is simply restored to its original condition. On the other hand, the picture developed by alkaline development, being imbedded in the film instead of being raised upon its surface, leaves its negative impression sunk into the emulsion after the removal of the silver by the acid. For this beautiful demonstration we are indebted to the late Colonel Russell (1865).

Although the foregoing explanation of the process of alkaline development is generally received and is probably in the main correct, there is one point which is not quite clearly made out, and I now bring it under notice for the same reason that I have dwelt upon other obscure points in the course of these lectures, viz. in order to incite investigation. The part of the process to which I refer is the reducing action of the nascent silver representing the invisible image upon the silver bromide with which it is in contact. In all probability this reducing action is the result of micro-electrolytic decomposition. All the conditions can in fact be reproduced by pressing particles of silver into a film of gelatino-bromide emulsion and developing with an appropriate developer without any exposure to light at all. Each metallic particle acts in this case as one element of a galvanic couple, and reduces the bromide with which it is in contact, the result being a corresponding number of dark spots dotted over the plate, which appear distinctly on brushing off the silver particles and fixing with thiosulphate in the usual way [M].

There are one or two other proofs that the building up of the silver image in alkaline development is the result of actions such as have been described, which may well occupy our attention for a few minutes in concluding. In the first place I will remind you of a striking experiment by Abney, who took a dry plate, exposed it in the camera, and then, before developing, coated one half of the plate with collodio-bromide emulsion and afterwards developed as usual. The image on the coated half was much denser than that on the uncoated half, clearly indicating that silver had been supplied from the film of collodion emulsion as well as from the bromide in the film of the original plate. The developing solution in this case soaks through the film of collodion emulsion before it can reach the invisible image. The latter then undergoes the usual reduction and the silver image is fed both from above and below, being sandwiched between the two films, both of which feed it with silver by micro-galvanic reduction. On separating the films an image

is found on the collodio-bromide film, which was not exposed, as well as on the original plate [N]. Then there is an equally striking experiment due to Dr. Eder, who coated a plate with a great thickness of gelatino-bromide emulsion and, after exposing and developing, found that the reduction of the silver bromide had taken place under the illuminated portions of the film throughout the whole thickness of the emulsion. In this case the silver picture is of course fed entirely by the reduction of the silver bromide beneath it, and as the light could not have exerted any influence on the lower portion of a layer of emulsion which was intentionally made so thick as to be opaque, the reduction which commenced at the surface must have extended downwards by the same process as that by which it spreads both upwards and downwards in the experiment of Abney's previously described. Such results as these are strongly suggestive, if not actually demonstrative of electrolytic action.

APPENDIX TO LECTURE V.

A (p. 144).—An ordinary uranium print (see Exp. I, Lecture I, p. 33) after exposure is cut into three strips, one of which is developed with potassium ferricyanide, the other with silver nitrate, and the third with gold chloride solution. After development the strips are pieced together so that the design appears tricoloured, brown, grey and purple.

B (p. 146).— Paper (well sized) is coated with Pizzighelli's "Cyanotype" solution prepared as follows :—

1. 20 grams gum arabic in 100 c.c. water.
2. 50 „ ammonio-ferric citrate in 100 c.c. water.
3. 50 „ ferric chloride in 100 c.c. water.

No. 1 . . . . . 20 c.c.
No. 2 . . . . . 8 c.c.
No. 3 . . . . . 5 c.c.

The mixed solutions if too thick can be cleared with a little dilute hydrochloric acid.

A sheet of paper thus prepared and allowed to dry is exposed under a design cut out in black paper to the electric light for about 10 minutes, and then cut into two strips, one of which is developed by being brushed over with a solution of potassium ferrocyanide and the other with a solution of the ferricyanide (about 15 per cent. solutions). The two strips are then pieced together so as to show the developed pattern half positive and half negative. The portion developed with ferrocyanide may require clearing by immersion in dilute hydrochloric acid.

C (p. 149).—A gelatine plate has a design painted on it with a solution of ferric or mercuric chloride, and is then given a brief exposure to the electric light. The plate is washed and then developed with ferrous oxalate developer, when the design comes out on a dark background, showing the retarding action of the ferric or mercuric salt.

D (p. 157).—The experiment is shown as described in the text, stripes being painted with thick gum-water on a sheet of glass which is supported vertically while a sand blast is directed on to its surface.

E (p. 159).—The experiment is shown as

described in the text, a solution of ferrous sulphate being added first to a solution of silver nitrate to show the formation of a precipitate, and then a stripe of the same solution painted on a sheet of paper moistened with silver nitrate, when a dark patch at once appears. For comparison a stripe of the solution is also painted on a sheet of paper coated with a silver haloid and free from excess of silver nitrate.

F (p. 161).—The action of restrainers, chemical and physical, is shown by the following experiment:— Equal quantities of a dilute solution of silver nitrate (about one per cent.) are placed in four beakers. To (1) is added about one-fourth its bulk of a five per cent. solution of gelatine; to (2) is added the same quantity of glacial acetic acid; to (3) is added the same quantity of dilute sulphuric acid; and to (4) is added the same quantity of distilled water. The four beakers thus contain the same bulk of a solution of silver nitrate and each contains the same quantity of silver. A dilute solution of ferrous sulphate is then run into each beaker from a burette, the same volume of solution being added to each beaker. The precipitation of reduced silver occurs at once in (4), less rapidly in (1) and (2), and least rapidly in (3).

G (p. 163).—Lermontoff's experiment can be made into a lecture demonstration by dividing a

glass cell with parallel sides into two partitions by means of a vertical brown paper septum, which must be cemented watertight to each side and to the bottom of the cell. The latter is then filled up in one partition with a two per cent. solution of silver nitrate, and to the same level in the other partition with a cold saturated solution of ferrous sulphate. The two solutions are connected by means of a bent silver wire which dips about half way to the bottom of the cell in each partition. On projecting an image of the apparatus on to the screen, the crystalline growth of silver is seen on the end of the wire in the silver nitrate solution. With a horizontal lantern the arrangement of the cell must of course be modified.

H (p. 164).—The paper is first coated with silver chloride in the usual way and, when dry, is striped with a weak solution of ammoniacal pyrogallate containing some sodium sulphite. As soon as the reduced stripes are distinctly visible the paper is washed, and then developed as described in the text. The whole experiment can be performed in a few minutes if the chloride-coated paper is previously prepared. It is better to moisten the surface of the paper with silver nitrate solution after washing and before development, instead of putting silver nitrate into the developer.

I (p. 165).—A glass plate is ruled with a

amond down its centre and then coated with col-dion and sensitized in the silver bath in the usual ay in red light. When sensitized the plate is ven a brief exposure to the electric light and then oken in half. One half is washed thoroughly in ater and then both this and the unwashed half are ultaneously developed with the iron developer, e washed portion of the plate after this treatment ing much lighter than the other.

J (p. 167).—The reducing power of ammoniacal rogallol was shown by the following experi-ents :—

1. An ammoniacal solution of silver nitrate was ixed with ammoniacal pyrogallol, an immediate recipitation of silver taking place.

2. Sheets of paper coated with chloride, bromide, nd iodide of silver were painted with stripes of the me solution of ammoniacal pyrogallol. A dark ripe of reduced silver appears in all three cases; ost strongly on the chloride, least strongly on the dide.

This last experiment serves well to illustrate the elative reducibility of the three haloids. The papers ust be free from excess of silver nitrate.

K (p. 168).—The experiment is performed as de-ribed in the text.

(p. 168).—The solubility of silver bromide n otassium bromide is easily shown by boiling

some freshly prepared silver bromide with a strong solution of potassium bromide and pouring the clear solution into a beaker of cold water.

M (p. 174).—A gelatine dry plate is moistened with water and some silver dust (prepared by reducing silver nitrate with ferrous sulphate) sprinkled over the surface. The metallic particles are pressed on to the film by passing a glass roller over the surface of the plate. A strong developing solution (ammonium pyrogallate or the ferrous oxalate developer) is then applied, and when the action has been allowed to go on for a sufficient time the plate is washed, the silver particles brushed off, and a fixing solution (thiosulphate) poured over the surface. After being fixed and washed the plate can be put into a lantern and its image projected on to the screen, when the darkened appearance of the portion which was under the silver dust is seen to greater advantage. It makes the illustration more striking if a design is stencilled out in a paper screen and the latter is applied to the surface of the plate before the silver dust is sprinkled on: the design then appears in the last stage as a dark granulation of the film. It is perhaps hardly necessary to say that the experiment must be conducted in red light up to the application of the fixing solution.

N (p. 176).—Abney's experiment can be shown

as a lecture demonstration by exposing a gelatine dry plate to diffused white light for a few seconds, and then allowing a streak of a previously prepared collodio-bromide emulsion to flow over the surface of the gelatine film. The streak of collodion emulsion is allowed to dry and then the plate is developed in the usual way (by ammoniacal pyrogallol and potassium bromide or by ferrous oxalate). The striped portion of the plate comes out darker than the background.

LECTURE VI.

Rapidity of Emulsion Plates partly due to Developer—Ferrous Oxalate Development—Collateral Phenomena of Development—The Developer a Quantitative Microchemical Test—Development of Chemical Reduction Product and of Pressure Marks—Relative Sensitiveness of the Silver Haloids in Different Processes—Relapse of the Invisible Image due to Reversed Chemical Change—Reversal of the Image or Solarisation—The Phenomenon a Recurrent one—Theory of the Process and the Function of the Sensitizer.

THE distinction between acid and alkaline development which was dwelt upon in the last lecture, and the different mode of action of the two kinds of developers, which was also explained, will enable us to appreciate more fully the reasons why our modern emulsion processes have such an enormous advantage in the

way of rapidity over the old wet-plate methods. The sensitiveness of the emulsion itself has, as has already been pointed out, a great deal to do with this rapidity, but a certain share must also be credited to the developer. In the wet-plate silver nitrate is present as a sensitizer. If we applied an alkaline developer to such a plate, the free silver nitrate would be at once reduced with results of a most disastrous nature to the picture; for this reason alkaline development cannot be used. In a gelatine emulsion plate on the other hand, as there is no free silver nitrate, we run no danger of fog from this source and a much stronger developer can be used. And not only can we use a stronger developer for this reason, but also because of the silver haloid particles being imbedded in a substance, gelatine, which acts as a physical restrainer, we can apply a reducing solution which would be strong enough to reduce the silver haloid directly to the metallic state were it not so protected. Thus there is a gain at both ends of the process—we have a more sensitive film to start with, and we

can use a strong developer after exposure. These are the reasons why instantaneous photography is now possible to every amateur.

It is unnecessary here to specify all the different kinds of developers which have been or which are in use. They all act in accordance with the principles of one or the other of the typical kinds of development. Of the numerous reducing substances which have been proposed as substitutes for ammonium pyrogallate, I need only mention the pyrogallates of potassium and sodium (with or without the addition of a sulphite,) hydroquinone (quinol), pyrocatechol, resorcinol, hydroxylamine, and certain organic ferrous salts. The latter are very largely used, a good type of the class being the ferrous oxalate developer introduced by Carey Lea in 1877; and to this, bearing in mind that it acts in the same way as the alkaline developers generally, we may fairly devote a little consideration.

Ferrous oxalate is a yellowish salt almost insoluble in cold water but readily soluble in a solution of potassium oxalate, owing to the

formation of a double oxalate which, in the solid form, has the formula $K_2Fe(C_2O_4)_2H_2O$ or $K_2Fe(C_2O_4)_2, 2H_2O$ according to its mode of preparation [A]. The developing solution contains as its active salt this potassio-ferrous oxalate, and the simplest way of preparing it is obviously to mix solutions of ferrous sulphate and potassium oxalate in the necessary proportions, as pointed out by Eder in 1879:—

$$FeSO_4 + 2K_2C_2O_4 = K_2Fe(C_2O_4)_2 + K_2SO_4.$$

In order to restrain the strong reducing power of the ferrous salt potassium bromide is added to the developer, its function being the same as in the alkaline pyrogallate. The chemical action of the ferrous oxalate developer is simple enough; the ferrous oxalate, which is the reducing substance, becomes oxidized to the ferric condition by the bromine which it withdraws from the reduction product, the latter being further reduced to metallic silver while the unaltered silver bromide, except where it is in contact with the

nascent silver, is not attacked owing to the presence of the restrainers (potassium bromide in the solution and gelatine in the film). The action between the ferrous oxalate and the reduction product thus resolves itself into the action of bromine upon ferrous oxalate in the presence of potassium oxalate :—

$$3Br_2 + 6FeC_2O_4 + 3K_2C_2O_4 = 3Fe_2(C_2O_4)_3 + 6KBr.$$

The addition of sodium thiosulphate, suggested by Capt. Abney in 1880, increases the activity of this developer, probably by reducing the ferric salt. There has been some discussion as to the chemical action of this accelerator and the equations given in the current manuals are generally erroneous. The thiosulphate is most probably oxidized to tetrathionate, as in the equation :—

$$\underset{\text{Ferric oxalate.}}{Fe_2(C_2O_4)_3} + \underset{\text{Sodium thiosulphate.}}{2Na_2S_2O_3} =$$

$$\underset{\text{Ferrous oxalate.}}{2FeC_2O_4} + \underset{\text{Sodium oxalate.}}{Na_2C_2O_4} + \underset{\text{Sodium tetrathionate.}}{Na_2S_4O_6}.$$

To the developers of this class belongs the ferrous citro-oxalate developer of Abney which is a mixture of potassio-ferrous oxalate and citrate with excess of potassium citrate.

Before leaving the theory of the action of photographic developers, there are certain collateral phenomena more or less connected with this theory which must next claim our attention. Let me in the first place present the action of a developer in another light—there is nothing like looking all round an explanation when we wish to assimilate it thoroughly. A photographic developer may be regarded as a microchemical test for the presence of traces of reduced silver haloid too minute to be detected by the eye. In the cases which have been considered, the infinitesimal trace of reduction product forming the latent image is of course produced by the action of light, and the developer, to push the analogy a little further, is not only a qualitative, but also a quantitative test, showing the quantity of reduction product formed on different parts of the exposed film by the varying amount of silver deposited. If the reduction product could be

formed on a surface of unaltered haloid by a purely chemical method without calling in the aid of light at all, the developer would reveal the presence of this product although nothing might be visible before its application.

Any reducing agent capable of reducing the silver haloids to the metallic state may be supposed to give as a first product the same compound as that which constitutes the invisible image, provided the reducing agent is applied in the presence of an excess of the silver haloid. Thus the alkaline hypophosphites or an alkaline solution of certain sugars, such as glucose or lactose, produce an invisible image on a surface of silver chloride, which image is capable of development in the ordinary way [B]. Such illustrations have been recently adduced by Carey Lea in support of the view that the invisible image is similar in composition to the coloured product formed by the action of light upon the silver haloid. Whether this argument will hold good or not in the light of future work, it is at any rate an interesting fact that, by the reducing action of certain chemical substances

upon the silver haloids, a compound can be formed which behaves towards developers in precisely the same way as the product formed by the action of light.

Not only can a developable image be produced by chemical means without the action of light, but it has been found that the same result can be produced simply by mechanical pressure. This fact was first made known in 1866 by Carey Lea for iodized collodion plates, and has been confirmed by Eder for bromized collodion, and by Warnerke and Abney for gelatine emulsion plates. The experiment is easily shown. It is only necessary to make marks with the rounded end of a glass rod on a gelatino-bromide plate, and then develop in the usual way without exposure to light. The pressure marks can be developed as though they had been formed by the action of light [C]. This must be considered as one of the obscure phenomena connected with photography. The explanation is by no means obvious, and it is for this reason that I have brought the subject under notice, because

I do not want you to go away with the impression that our photographic theories are so complete as to leave no room for further research. Moreover I have a suggestion to offer which may or may not be fruitful. Investigations which have been made of late years by Spring and others, seem to show that chemical change can be induced in mixtures or compounds by submitting them to great pressure. It is not improbable therefore that such unstable compounds as the silver haloids in the presence of sensitizers, should undergo a minute amount of decomposition by strong mechanical pressure, the decomposition being so infinitesimal as to be revealed only on application of that most sensitive of micro-chemical tests, the photographic developer.

There is another point in connection with the use of the silver haloids for photographic purposes which we are now in a position to deal with; that is, the relative sensitiveness of the three haloids in different processes. From the thermochemical data you know that the order of sensitiveness, as

measured by the stability of the three compounds, might be expected to be iodide, bromide, chloride. The order of darkening by photo-decomposition is the reverse, but this is an accident connected with the colour of the reduction products. The order of reducibility of the three compounds is the same as the order of darkening, viz. chloride, bromide, iodide [D]. The fact that the order of reducibility is the reverse of the order of stability may appear somewhat anomalous to those who are unaccustomed to consider these problems, but a little explanation will clear up this point. In a general way the reduction of a silver haloid may be regarded as the action between the halogen and hydrogen. Now the heat of formation of the three haloid hydracids is in gram units:—

H,Cl	+ 22,000
H,Br	+ 8,440
H,I	− 6,040

It is not surprising therefore that silver chloride ıould be the most ready to part with its chlorine) reducing agents. The practical application of

these considerations is seen in the comparative facility with which the haloids can be developed by the alkaline method, when used in the form of dry plate films. The iodide requires a stronger developer than the bromide, and the latter a stronger developer than the chloride. A developer which is just strong enough to develop a bromide plate to perfection, might fog a chloride plate owing to the easier reducibility of the latter haloid. These remarks of course apply only to alkaline developers which have a tendency to reduce the silver haloids directly; an acid developer, I need hardly remind you, has no tendency to reduce the silver haloids, but acts by reducing the silver nitrate present as a sensitizer.

In actual photographic processes the normal order of sensitiveness of the haloids is not always maintained, a fact for which we shall be quite prepared when we consider the numerous complicating influences introduced by the sensitizer, the vehicle, or the state of molecular aggregation of the haloid. In the wet collodion process the sensitiveness is normal, *i.e.* the iodide is the most

sensitive and the chloride the least sensitive. In gelatine emulsion processes the bromide is the most sensitive; more so than the iodide, even when the latter is submitted to the ripening process which confers upon the bromide its extreme sensitiveness. The order for gelatine emulsion appears to be bromide, chloride, iodide.

Such facts as these are at present very difficult to interpret, not only because of the complexity of the conditions which determine sensitiveness, but also because of our ignorance of the weight to be attached to each condition. Thus the bromide may be more sensitive than the iodide in gelatine emulsion because the vehicle is a better sensitizer for the former. In other words gelatine may be a better bromine absorbent than it is an iodine absorbent, so that the system AgBr + gelatine may be more sensitive than the system AgI + gelatine. Then again in comparing the haloids in the state of emulsion, we do not know whether the salts are strictly comparable as far as regards their state of molecular aggregation—we have no means

of knowing whether the state of molecular complexity is the same in the two cases, and till this is known we are unable to form any opinion as to the effect of the molecular condition upon the sensitiveness of the haloid. Chemists will follow me when I say that we are in the dark as to whether the silver bromide in a gelatine emulsion is in the condition AgBr, Ag_2Br_2, Ag_3Br_3, or $Ag_n Br_n$, and in comparing such an emulsion with a silver iodide emulsion we may in reality be comparing two molecules of a quite different order. Furthermore, the action of the developer must be taken into consideration; the bromide, being more reducible than the iodide, is susceptible to a weaker developer and thus has the advantage from this point of view. This discussion will be instructive, if only as showing how complex are the phenomena with which the photographic chemist has to deal, and how much has yet to be learnt before some of the most familiar facts can be properly understood.

Closely connected with the phenomena of

development and with the general theory of photographic action, is the disappearance or destruction of the invisible image, a subject which may now conveniently claim a share of our attention. It is a familiar fact to all who have had experience of photographic processes, that the latent image cannot be preserved for an indefinite time. The period during which the image can be retained in a developable state varies in different processes ; from a few hours in the case of Daguerreotype to two years or more in the case of a good gelatine plate. With the lapse of time the developable image gradually fades out in all processes, and we have now to consider the explanation of this phenomenon.

Looking at the invisible image as a photo-reduction product we shall be prepared to admit that such a compound, like all reduced products, is susceptible of oxidation [E]. In accordance with this view of the composition of the invisible image, it is found that the latter can be destroyed by oxidizing agents, using this term in a wide sense. This fact, I need hardly stop to point out, gives

additional support to the view that the invisible image is a chemical product and not a mere physical modification of the haloid. It is obvious that the most direct way of regenerating the reduced haloid—that is to say of restoring the lost halogen to the film—is to apply a further quantity of the halogen itself. Of course it is not essential that the same halogen should be applied, because you can readily understand that there may be a series of chemically analogous reduction products —oxyhaloids or whatever they may be—in which one halogen may replace another. Thus the photo-reduction product of silver chloride would be destroyed by bromine with the formation of a mixture of silver chloride and bromide, so that the halogens are among the most effective agents for destroying the invisible image. If for instance an exposed Daguerreotype plate is submitted to the vapour of bromine or iodine, no picture can be obtained on development—the halogen has undone the work done by light. The phenomenon is precisely analogous to that which occurs when silver chloride is exposed to light in a closed

vessel. You have seen in a former lecture that chlorine is evolved when this haloid becomes coloured by photo-decomposition. If the chloride is sealed up in a tube the halogen cannot escape, and when the tube is removed from the influence of light the action slowly becomes reversed; the liberated chlorine reacts with the reduction product and regenerates silver chloride. A tube of the latter slightly darkened by light and put away during the night will be found to have become white again by the morning. Oxidizing agents such as nitric acid, the chromates, permanganates, metallic perhaloids, &c., are equally effective in destroying the invisible image [F].

The next step is to connect these facts with the spontaneous relapse of the invisible image—a task which, in the absence of precise knowledge concerning the chemical composition of the reduction product, is by no means an easy one to perform. Since oxidizing or halogenizing agents are known to destroy the invisible image, it is but natural to suppose that the disappearance of the latter is due to gradual oxidation or to

rehalogenization. There can be but little doubt that this explanation is true in a general way, although it is difficult in many cases to follow the exact course of the chemical changes which occur. For this reason it is impossible to group all the causes of relapse in the different processes under one general chemical reaction, but the broad principle may be sketched in outline. The reduction of a silver haloid by light is not, as I need hardly remind you, a simple case of dissociation—the reduction takes place at the expense of the oxidation or halogenization of the sensitizer, whatever the latter may be. Chemists will know what is meant when I say that halogenization and oxidation are often synonymous. The liberated halogen for instance may not attack the sensitizer directly, but water may take part in the reaction, the halogen decomposing the latter and liberating the oxygen which, in the nascent condition, is absorbed by or oxidizes the sensitizer :—

$$Cl_2 + H_2O + \text{sensitizer} = 2HCl + (\text{sensitizer oxidized}).$$

In other cases again the halogen may be directly

absorbed by the sensitizer, forming substitution or additive products. Whichever of these modes of action takes place, it is clear that in every photographic process we have formed in the same film reduction product and oxidation product. Now when the stimulus of light is withdrawn there is no further liberation of halogen—the *outward tension*, if I may use such an expression, of the halogen ceases, and we have reduced product in contact with oxidized product, an unstable system capable of reacting chemically. Such a reaction would take place but slowly, partly owing to the solid condition of the reacting substances and partly depending on the stability of the oxidized product, but as the reaction goes on the reduced product would gradually become oxidized, while the oxidized product would at the same time become reduced—the film would be gradually restored to its original condition; the latent picture would fade away. In such cases it is clear that we have what may be considered as a reversed chemical change.

The explanation which is here submitted is no

doubt true in the abstract, but I am afraid it may be "in the air" as far as concerns those who are accustomed to deal with photography from its practical side only. Let me endeavour to illustrate the explanation by applying the principles laid down to some of the typical processes. To begin with the simplest case—the Daguerreotype plate. After exposure we have a reduced product poorer in iodine than the original silver iodide by a certain amount of that halogen. The iodine set free may be regarded as combined, wholly or partly, with the excess of silver iodide, a possibility for which you have been prepared in a former lecture (p. 151). We thus have reduction product in contact with iodized silver iodide. But the latter is a comparatively feeble compound, and as soon as the plate is withdrawn from the influence of light it begins to give back its iodine to the reduction product. The chemical tension which is thus produced in the film by the action of light gradually runs down in the dark—the de-iodized portion of the film is re-iodized and the invisible image is obliterated.

Consider in the next place the wet collodion process. The liberated iodine is here absorbed by the sensitizer (silver nitrate), possibly in accordance with the equation:—

$$3I_2 + 6AgNO_3 + 3H_2O = 5AgI + AgIO_3 + 6HNO_3$$

In the absence of the external stimulus which, as long as it acts is tending to set free iodine, it is not improbable that the mixture of oxidizing substances in contact with the reduced product gradually react in the reverse manner, liberating iodine and rehalogenizing the reduced product, *i.e.* destroying the invisible image according to the reaction:—

$$5AgI + AgIO_3 + 6HNO_3 = 6AgNO_3 + 3H_2O + 3I_2 \text{ (absorbed).}$$

Whether this represents the actual course of events or not must be decided by future work, but you will readily understand that the reduction product could not remain for any great length of time in contact with nitric acid and an iodate

without becoming oxidized. It is indeed known that nitric acid alone is capable of destroying the latent image [G]. From these considerations it follows that a wet collodion plate should retain its impression longer after exposure if the film were washed free from the secondary products of photo-decomposition. This has been found to be the case. It is obvious also that the persistence of the image would be prolonged if the formation of highly oxidized products were prevented *ab initio*. The truth of this deduction has been verified by Professor H. W. Vogel, who exposed an iodized collodion plate under sodium sulphite, a reducing agent which effectually prevents the formation of an iodate or of nitric acid :—

$$I_2 + Na_2SO_3 + H_2O = Na_2SO_4 + 2HI$$

The invisible image is retained by such a plate for a much longer time than when silver nitrate is the sensitizer.

In cases such as have been now dealt with, where the chemical action of the sensitizer is

obvious, or where it can be conjectured with some degree of probability, the cause of the disappearance of the latent image can be represented chemically with more or less plausibility. But when we come to deal with sensitizers like tannin or gelatine in the dry plate processes, the explanation is much more difficult owing to our ignorance of the nature of the halogenized products, and we can at present only advance by analogy. Thus the halogenized gelatine for example may in the absence of light, and in contact with the reduced silver haloid, gradually rehalogenize the latter. It is generally believed also that atmospheric oxygen (or ozone) plays a part in the obliteration of the invisible image—in fact it has been proved by experiment that ozone acts like other oxidizing agents in this respect. The destruction of the image may in such a case be due to indirect rehalogenization; that is to say the oxygen or ozone may oxidize the halogenized sensitizer and so liberate the halogen, which then ttacks the reduction product. The longevity f the impression on dry gelatine plates may

be due to the fact that the halogenized sensitizer being in the solid state can part but slowly with its halogen, while at the same time the action of the air is for the same reason retarded. Nor must it be forgotten that the particles of the reduction product are actually imbedded in the vehicle instead of forming a surface film as in the collodion wet plate.

Among the reagents which destroy the latent image and of which the mode of action is by no means clear, are the mineral acids. Nitric acid no doubt acts simply as an oxidizer, but the haloid hydracids cannot act directly in this way. It is extremely probable that there is in the case of these acids a film-reaction in which the acid is decomposed by being in contact on one side with reduction product, and on the other with atmospheric oxygen, as shown in the following scheme:—

$$\text{Reduction product} + 2\left\{\begin{matrix}\text{HCl}\\\text{HBr}\\\text{HI}\end{matrix}\right\} + \text{O} = \text{Silver}\left\{\begin{matrix}\text{Chloride}\\\text{Bromide}\\\text{Iodide}\end{matrix}\right\} + \text{H}_2\text{O}$$

If for the moment we assume that the reduction product is actually an oxyhaloid, the mineral acids might be supposed to act directly upon such a compound in accordance with the equations :—

$$Ag_4OI_2 + 2HNO_3 = 2AgI + 2AgNO_3 + H_2O$$
$$Ag_4OBr_2 + 2HI = 2AgI + 2AgBr + H_2O$$

But this explanation does not appear to hold good because it carries with it the implication that the silver haloids should not undergo photo-decomposition when immersed in mineral acids, and that the reduction products when formed should be decomposable by such acids. Experiment disproves this deduction ; darkened silver chloride or bromide can be formed when the haloid is suspended in hydrochloric or hydrobromic acid, and the darkened product is not bleached by immersion in these acids, even when the latter are of sufficient strength to destroy the latent image. It appears that the acids have no action in the cold on the reduction product in bulk when this product is excluded from contact with the air, as is the case when it is suspended

in the acid solution. But when the reduction product is spread over a plate in the form of a thin film the acids readily exert a destructive action, and that is the reason why it seems so probable that atmospheric oxygen takes part in the process.[1]

The explanation of the destruction or spontaneous disappearance of the latent image which has been submitted will enable us to advance a step towards the consideration of another phenomenon which has long been a puzzle to practical photographers—I allude to the reversal or solarisation of the image. Let us approach this subject from the experimental side, interpreting the results as we proceed in the light of our present knowledge of the conditions necessary for the destruction of the reduction product. If we take a sheet of paper coated with silver chloride and darken it by exposure to light, we have a surface of reduction product which can of course be

[1] It is not improbable that the halogenized sensitizer (or vehicle) may give back its halogen when acted upon by mineral acids in the presence of the reduction product. The destructive action of these acids may thus be due to indirect rehalogenization.

bleached by any substance which acts as a re-halogenizing agent [H]. This experiment is obviously nothing more than a visible demonstration of that which occurs when the invisible product is treated with similar reagents (See exp. F of this lecture) and requires no further explanation. Now it was observed by Lassaigne in 1839, and about the same time by Sir John Herschel, that a solution of potassium iodide also bleaches the darkened product of photo-decomposition under the influence of light, a fact which was further investigated by Robert Hunt, Fox Talbot and others [I]. This result is also easily explicable if we bear in mind the fact alluded to in a former lecture (p. 25), that potassium iodide is susceptible of photo-oxidation by atmospheric oxygen with the liberation of iodine. In Lassaigne's and Herschel's experiment we have potassium iodide in contact with a reducing agent on one side and with atmospheric oxygen on the other; all the nditions are favourable for the decomposition the potassium iodide—the latter is the photo-nsitive salt and the reduction product acts

towards it as a sensitizer, thereby becoming re-halogenized and bleached. Potassium bromide and chloride act in a similar way but more slowly, because these salts are more stable in the presence of light and oxygen than the iodide [J].

The point of greatest importance to us in connection with these facts is the strict analogy which obtains between the bleaching or reversing action of the alkaline haloids and the destruction of the reduction product, visible or invisible, by oxidizing or halogenizing agents. The only difference is that the latter act at once upon the reduction product in the dark, while the former act only under the stimulus of light;[1] the mineral acids, &c. are in the one case chemical reagents, while the alkaline haloids are in the other case

[1] It has been observed that potassium iodide to some extent bleaches darkened silver chloride paper even in the dark, but this preliminary action is probably due to the formation of a certain quantity of the lighter coloured iodo-reduction product by double decomposition. Assuming the oxyhaloid formula the reaction would be:—

$$Ag_4OCl_2 + 2KI = Ag_4OI_2 + 2KCl.$$

This would be analogous to the well-known decomposition of silver chloride by potassium iodide.

photochemical reagents. Consider a concrete example:—

A sheet of paper coated with a silver haloid, say the chloride, is exposed to light for a few seconds and a stripe of hydriodic acid painted on it. On washing and developing, the portion acted upon by the acid remains white, because the reduction product has been rehalogenized in accordance with principles with which you are familiar. In the next place a similar sheet of paper is darkened by exposure, then painted with a stripe of potassium iodide solution and again exposed to light. This is the Lassaigne-Herschel experiment, and you know what happens—the portion of the paper painted with the potassium iodide becomes bleached. *The potassium iodide in the presence of light behaves exactly like the hydriodic acid in the absence of light*, and the final result, so far as concerns the reduction product, is the same in both cases.

I need hardly stop to point out the practical application of this bleaching action of potassium iodide; but you will readily understand that if a

sheet of darkened silver chloride paper is coated with a solution of potassium iodide and exposed under a design, we shall have a print in which those portions of the surface protected from the light remain dark while the exposed portions become bleached. A process for obtaining positive prints from engravings, &c. has been based on this principle [K].

From the action of such reversing agents as the alkaline haloids, which it must be remembered depend upon the co-operation of light and atmospheric oxygen, we are naturally led to the destruction of the latent image on the plate itself without the extraneous aid of a reversing agent. This phenomenon has long been familiar under the name of "solarisation," because it is an effect produced by over-exposure, especially in the presence of strong sunlight. Let me first describe the facts in outline. If a sensitive plate is exposed to strong light, the latent image gains in intensity up to a certain point and then begins to fall off. Thus in an over-exposed landscape the sky may come out light instead

of dark in the negative, so that on printing we should have a reversal of natural effect and the sky would appear black instead of white. No process is altogether free from this defect, but speaking generally it may be said that the more sensitive the plate the greater the tendency to become solarised by over-exposure. This effect being the result of too strong an illumination upon certain portions of the plate, it will be apparent that the high lights in a picture may by this means become reversed and give an unnatural distribution of light and shade in the print. The general appearance is well seen in the silver print which I am enabled to exhibit through the kindness of Mr. John Spiller, by whom the negative was taken a great many years ago on a wet collodion plate. It will be seen that the trees have come out almost white against a dark sky in the positive.

The conditions leading to solarisation, and the peculiarities in the phenomenon itself, have been studied by many observers, and especially by Abney, but beyond the establishment of the very

plate might give an ordinary negative with a weak developer, and a reversed negative (positive) with a strong developer. Then again it has been found, chiefly through the researches of Abney, that oxidizing agents facilitate reversal, while reducing agents retard it or prevent it altogether. Oxidizing agents and preliminary exposure act in the same way. A plate washed with a chromate, permanganate, &c., is easily reversed, while a similar plate washed with a nitrite or sulphite is not susceptible of solarisation with ordinary exposures. Lastly, it must be borne in mind that the phenomena of reversal go on invisibly in the film because the amount of reduction product formed never reaches a visible quantity. Eder states that a gelatino-bromide plate may be exposed for a sufficient time to produce strong solarisation on development with ferrous oxalate, without a trace of discoloration being apparent. Such are the facts which have now to be dealt with from a chemical point of view.

At the outset we are as before confronted with our ignorance on two points, the chemical com-

position of the reduction product and of the halogenized sensitizer, so that any theory of solarisation can at present be expressed only in very general terms. Now the first idea to be grasped is that reversing agents like potassium iodide, which acts upon the visible product of photo-reduction in the manner previously explained—and I will refresh your memories by repeating the equation :—

$$4KI + 2H_2O + O_2 = 4KOH + 2I_2,$$

act in a precisely similar manner upon the invisible product, *i.e.* the latent image. Potassium iodide for instance can be used as an artificial solarising agent. Poitevin showed as long ago as 1859 that it is possible to get a positive on glass instead of a negative by means of this substance. If we take an iodized collodion plate, sensitize it, and then expose to diffuse light for a few seconds, we get a film of reduction product on the surface of unaltered haloid. If the plate is then washed to remove silver nitrate, coated with a film of potassium iodide solution, and then exposed in the camera for three or four times the period

necessary to get a good negative, the most strongly illuminated portions of the film become rehalogenized, while the deep shadows remain as unaltered reduction product, and the intermediate shades get partially rehalogenized. On development the high lights therefore come out white, the shadows dark, and the intermediate shades of an intermediate tint —in other words we get a positive instead of a negative. This experiment is for the invisible image what the Lassaigne-Herschel experiment is for the visible product of photo-reduction [M].

The principle revealed by this experiment of Poitevin's is a very simple one—it just amounts to this :—that any photochemical reagent capable of liberating a halogen under the joint influence of light and atmospheric oxygen, is able to act as a reversing agent by rehalogenizing the invisible image. It is for this reason that an excess of potassium bromide acts detrimentally if left in an emulsion, because it diminishes the sensitiveness of the latter. That is why it is essential to remove this salt by washing, as pointed out in a former lecture (p. 123).

In ordinary cases of solarisation, where no special photochemical reagent is added to the film, there must be something present which plays the part of such a substance. It is, I believe, to the sensitizer that we must look for the whole explanation of the phenomenon. How the sensitizer acts will of course depend upon the particular process; the chemical reactions which take place may be at present quite impossible to follow out, but it may be fairly asserted that when the sensitizer is halogenized up to a certain point it begins to react with the reduction product, the reaction being promoted by the presence of oxygen and moisture, and taking place even in the presence of light. We thus connect solarisation[1] with those other

[1] The observation of Sabatier, that a collodion wet plate becomes reversed if, towards the end of development, daylight is suddenly admitted to the room, relates to cases of what may be called pseudo-solarisation, which do not come under consideration in the present category. The explanation of this kind of reversal was given by Seely in 1860. It depends simply upon the fact that if the surface of a plate is strongly illuminated during development, the portions of the picture already developed, being represented by a more or less opaque film of metallic silver, act as a screen and prevent the further action of light on the portions of the film beneath them, whereas the undeveloped portions of the

phenomena which have led us up to its consideration ; with the destruction of the invisible image by oxidizing or halogenizing agents, with the destruction of this image in the dark by the haloid hydracids plus atmospheric oxygen, and with the spontaneous relapse of the latent picture in the dark by the action of the halogenized sensitizer itself, more or less aided by the oxygen of the air. Let us see how far this explanation will carry us when applied to special cases.

Imagine a collodion wet plate exposed to the continued action of strong light. The silver iodide goes on losing iodine, while the sensitizer (silver nitrate) concurrently absorbs the halogen with the formation of oxidized products, probably silver iodate and nitric acid. The amount of these oxidized products at length becomes so great that they begin to react with the reduction product — the action

surface are susceptible of photo-reduction to an extent proportional to the intensity of the light which falls upon them. If, as in the observation referred to, the light which is thus admitted is stronger than that by which the latent picture was first formed, it is obvious that the undeveloped portions of the surface will come out darker than the first developed portions, *i.e.* the picture will be reversed.

begins to reverse itself, and a certain amount of the work done by the first action of light becomes undone. If at this point we develop the plate it would be lighter than if we developed after a shorter exposure. We have arrived at the first neutral stage. Supposing the action to continue we have the system,

$$\text{Reduction product} + AgIO_3 + HNO_3 + O_2,$$

still undergoing chemical change, the reduction product becomes more and more halogenized and oxidized till the whole action of the light is reversed. At this point we have reached the stage of true reversal, and the plate on development would give no result. But affairs have now arrived at the same state as when the experiment was started; we have normal haloid under a film of silver nitrate again, this sensitizing salt resulting from the reduction by the reduction product of the oxidized products first formed, and the cycle recommences. After a further exposure we should get a negative of the second order on development, and so on.

Consider again the solarisation of a gelatino-

bromide plate. The gelatine becomes more and more brominated till it begins to rehalogenize the reduction product; then the latter becomes more or less converted into normal bromide, till the original state of affairs is restored and the operations begin to repeat themselves. The whole process is nothing more than an accelerated cyclical repetition of that which occurs in the spontaneous disappearance of the latent image in the dark.

So far the explanation may be considered to hold good in a general way, but there are other points which have to be brought into harmony with the theory. Perhaps the most obscure of these is the part played by oxygen and by oxidizing agents, but the obscurity here arises from our ignorance of the chemical nature of the halogenized sensitizer, and this, by the way, is one good reason for dwelling upon it. It may be safely asserted that oxidizing agents act inimically to the liberation of halogen. I may remind you of some of our earliest experiments in this direction. A sheet of paper coated with a silver haloid and exposed to light remains unacted upon at those

portions of its surface which have been painted with oxidizing solutions, such as mercuric or stannic chloride, potassium dichromate, &c., (Exp. A Lect. III. p. 100). Now any substance which is inimical to the liberation of halogen cannot act as a sensitizer, and if in contact with a substance which can act in this capacity it will lessen the sensitizing action of the latter by diminishing its halogen absorbing capacity. Thus a sensitive plate in an oxidizing solution, or washed over with such a solution, is easily solarised, because the sensitizer, being in contact with the oxidizing agent, can hold a less charge of halogen—it parts more easily with its halogen to the reduction product, and so more readily rehalogenizes the latter.

Whether the oxygen of the oxidizer actually becomes absorbed by the sensitizer, and replaces the halogen which the latter has passed back to the reduction product, must depend upon the nature of the sensitizer. Evidence is not wanting that such oxidation does actually occur. Thus Abney states that if a gelatino-bromide plate is exposed till a visible image is apparent, the portions of the film corre-

sponding to the image do not swell up when the plate is immersed in water.[1] Such a property is well known to be conferred upon gelatine by oxidizing agents, but this interpretation is complicated by the fact that brominated gelatine acts in a similar way. There is however another consideration which tends to show that oxygen is actually absorbed by the sensitizer during the process of reversal on dry plates, and that is the fact that the intervals which separate the successive phases are not uniform but of continuously increasing length. If the process were simply a case of alternate bromination and debromination of the sensitizer, the intervals might be expected to be uniform. The fact that the intervals lengthen points to the using up of something in the sensitizer: it indicates the exhaustion of the halogen-absorbing power of the latter, and the only extraneous source of such enfeeblement is the oxygen of the oxidizing solution or of the atmosphere.

These considerations will enable us to strip the

[1] *Treatise on Photography*, 5th ed. p. 309.

phenomenon of spontaneous reversal of some of its mystery. We must look upon a sensitive plate —say gelatino-bromide—as a film of silver bromide imbedded in a bromine-absorbing substance, and bathed on its surface by atmospheric oxygen. When exposed to light the vehicle becomes brominated up to a certain degree of saturation; complex bromo-derivatives, or additive compounds, or oxidized products are formed, and these at length begin to react with the reduction product aided by the external oxygen. The process may be regarded as analogous to the destruction of the latent image by the haloid hydracids, and indeed it is not improbable that some hydrobromic acid is actually formed by the bromination of the gelatine, and takes part in the process of reversal. The course of events will be understood from the following scheme:—

$$\text{AgBr} + \text{Gelatine} + \text{O} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{ First stage.}$$

$$\text{Reduction product} + \left\{\begin{array}{c}\text{Brominated gelatine}\\ + \text{ oxidized products}\\ + \text{HBr}\end{array}\right\} + \text{O} \quad \text{First negative.}$$

$$\left.\begin{array}{c}\text{gBr} + \text{oxidized reduction product}\end{array}\right\} + \left\{\begin{array}{c}\text{Debrominated}\\ \text{and deoxidized}\\ \text{products}\end{array}\right\} + \text{H}_2\text{O} \left\{\begin{array}{c}\text{First neutral}\\ \text{stage and}\\ \text{reversal.}\end{array}\right.$$

From these explanations the other facts connected with solarisation follow as necessary consequences. It is obvious that a highly sensitive plate would halogenize its sensitizer more rapidly than a less sensitive plate ; *that is why solarisation occurs more readily in the most sensitive processes.* We must be prepared to admit that a vehicle capable of becoming highly charged with halogenized products might act without the aid of oxygen, and it has accordingly been found that a gelatino-bromide plate can be reversed by prolonged exposure in a neutral liquid (benzene) which prevents access of air.[1] Then again we see that a substance capable of neutralising the effect of external oxidation, and of preventing the accumulation of too large a quantity of halogenized products in the sensitizer, must act antagonistically to reversal. Such is the action of reducing agents on the film. So also it is now evident that any process which partly halogenizes the sensitizer

[1] "If a plate be exposed in benzene, however (a liquid which does not permeate through the gelatine), the phenomena are still existent." Abney's *Treatise on Photography*, 5th ed. p. 309.

must accelerate the rate of reversal, because the partially halogenized sensitizer is nearer its saturation point, *i.e.* the point of halogenization necessary for the reversal of the reaction to set in. *This is why a preliminary exposure of the plate is so favourable to solarisation.*

The last phase of the subject demanding our attention is the part played by the developer—we have to follow out its action upon a solarised plate as compared with its action upon a normally exposed film. When reversal takes place, the portions of the film where the greatest action has been exerted, *i.e.* the strongest lights, consist of the most highly halogenized (and oxidized) portions of the sensitizer or vehicle. At the same time, owing to the length of exposure, the silver haloid over the whole surface of the plate is to some extent decomposed. Now the general result of halogenizing or oxidizing such a vehicle as collodion or gelatine is to harden it, and make it less pervious to aqueous solutions; the greater the amount of halogenization the less pervious does it become [N]. When therefore the developing solution is applied, the amount

of silver deposited or reduced on any part of the film is determined by the readiness with which this solution can get at the reduction product—where the sensitizer is most highly halogenized not only is the developer less able to attack the reduction product, but there may be in some cases actually less of the latter present owing to its partial destruction by the reversing action. On the other hand, the portions of the film which have received less illumination are more pervious and respond sooner to the developing action; these portions come out dark, while the solarised portions remain light; the image is reversed on development. In ordinary development the density of the silver deposit is proportional to the amount of reduction product formed; in a solarised film the density of the silver deposit is inversely proportional to the degree of halogenization of the sensitizer. This is doubtless the chief function of the developer, but the action is further complicated by the element of time having to be taken into account.

During the process of development the solarised portions must be regarded as also undergoing reduc-

tion (or accretion) to some extent—it is entirely a case of relative rates of action. With a strong developer the action upon the unreversed portions is exerted at once, because these are the most pervious to the solution. A weak developer, on the other hand, cannot attack the relatively small amount of reduction product on the unreversed portions, but as it must act longer to produce any effect at all it has time to penetrate the less pervious solarised parts of the film, and to reach the relatively larger amount of reduction product which they contain. Hence a weak developer may give a negative, and a strong developer a positive on development of an over-exposed plate. This, I may remind you, is one of the well-known characteristics of the phenomenon with which we have been dealing.

I have been tempted to dwell at some length upon these residual phenomena, both because of the promising fields of investigation which they offer to the scientific student, and because of their importance in the general theory of photographic action. There has been too great a tendency

hitherto to limit attention to the sensitive silver haloid, as though this were the agent in chief. In future we must look upon the sensitizer or vehicle with which it is associated as playing an equally important part. The silver haloid and the sensitizer are two correlated factors which cannot be considered apart in any of our photographic processes. A ray of light falling upon a sensitive plate is like the motive power driving a dynamo-machine which is feeding a storage cell. When the charge of the latter has reached a certain point it is capable of reversing the motion of the system, and of converting the dynamo into a motor. The sensitizer plays the part of such a storage cell; when it becomes charged, *i.e.* halogenized, to a certain amount, the chemical energy stored up in it begins to run down and reversal takes place.

APPENDIX TO LECTURE VI.

A (p. 187).—A solution of potassium oxalate is added gradually to a solution of ferrous sulphate in order to show the precipitation of ferrous oxalate and its solution in excess of potassium oxalate.

B (p. 190).—An alkaline solution of milk-sugar is painted in stripes on the surface of a sheet of silver chloride paper, and after being allowed to act for a few minutes (at the ordinary temperature of the room) the paper is well washed, and then brushed over with a ferrous oxalate developing solution. The stripes which have been reduced by the milk-sugar, although before development undistinguishable from the rest of the surface, come out intensely dark.

C (p. 191).—The experiment is performed as described in the text. Care must be taken not to tear ıe film. After developing and fixing, the pressure ıarks can be projected on the screen by means f the lantern.

D (p. 193).—Repetition of Exp. J, 2, Lect. V.

E (p. 197).—Exp. E, Lect. I. is repeated, the portion of the solution exposed to light being divided into two parts before the addition of the ferricyanide. There are thus three vessels, (1) containing unexposed solution, (2) and (3) containing exposed solution. To one of the latter some chlorine water is added, and then ferricyanide to all three. The chlorinated and the unexposed solutions give the same result, showing that the chlorine has undone the work done by the light.

F (p. 199).—A sheet of paper coated with silver bromide is sensitized with a solution of sodium nitrite, or with silver nitrate, and exposed to the electric light till it just shows faint signs of darkening. The paper is then well washed, and three or four stripes painted on it with various oxidizing solutions, such as bromine water, potassium dichromate, mercuric chloride, potassium permanganate (acidified), &c. After the reagents have been allowed to act for a few minutes (in red light) the paper is again well washed, and then developed with ferrous oxalate developer. The stripes come out light on a dark ground, showing the destruction of the reduction product by the oxidizing agents.

G (p. 204).—A plate is coated with iodized collodion and sensitized in the silver nitrate bath in red

light in the usual way. A few seconds' exposure to diffuse white (electric) light is then given, after which one half of the plate is immersed in nitric acid (one part 1·4 sp. gr. acid and two parts water), then withdrawn and washed, re-dipped in the silver bath, and developed by iron developer. The portion of the plate acted upon by the nitric acid remains undeveloped, showing the destruction of the invisible product of photo-reduction.

H (p. 209).—A sheet of paper coated with silver chloride is exposed to diffuse white light till distinctly darkened, and then painted with stripes of chlorine water and a solution of iodine in potassium iodide in order to show the bleaching action of these substances.

I (p. 209).—The darkened surface of the paper used in the last experiment is painted with another stripe of potassium iodide solution and exposed to white light till bleached. This experiment serves well to show the similarity in the action of the potassium iodide under the influence of light, and of the chlorine water and iodine solution in the absence of light.

J (p. 210).—A sheet of paper coated with silver chloride and darkened as before is painted with ripes of solutions (about 5 per cent) of potassium loride, bromide and iodide, and then exposed to rong white light till the iodized stripe appears

yellowish white. The bromide stripe, although lighter than the ground colour, is then darker than the iodide, while the chloride stripe has hardly bleached at all.

K (p. 212).—A sheet of darkened silver chloride paper is sensitized with a 5 per cent solution of potassium iodide, and exposed in a moist state under a design stencilled out in a black paper screen. On removing the screen the design comes out light on a dark ground. The addition of a little acid to the potassium iodide solution accelerates the action.

L (p. 215).—Bennett's experiment can be shown by placing a sliding screen of black paper over a gelatino-bromide plate, and giving different stripes of the surface exposures to the electric light for periods varying from two or three seconds to ten or fifteen minutes. On development by ferrous oxalate the darkness of the stripes increases up to a certain exposure, and then falls off again. It is impossible to name the precise period of exposure necessary to show the effects of reversal, as this varies in different plates. An instantaneous exposure of the whole surface of the plate to diffuse light hastens the experiment.

M (p. 218).—An iodized collodion plate is sensitized in the silver bath, exposed for a second or two to diffuse white light, and then washed with

water (in red light). One half of the plate is then dipped in a 5 per cent solution of potassium iodide (acidified with dilute nitric acid), and the whole surface again exposed to white light for about a minute. On washing, re-dipping in silver nitrate, and developing with the iron developer, the portion of the plate which has been dipped in the potassium iodide solution comes out much lighter than the other portion.

N (p. 227).—A design is painted with weak bromine water on the surface of a gelatino-bromide plate (in red light). After remaining in contact with the film for a minute or two the plate is well washed, and then exposed to diffuse white light for a few seconds. On development by ferrous oxalate the design comes out lighter than the background.

LECTURE VII.

Composition of White Light.—The Spectrum.—Visual Intensity and Photographic Intensity.—Colours of Natural Objects.—Spectrum Photography.—Graphic Representation of Intensity.—Action of the Spectrum on the Silver Haloids.—Concurrent Reversal in Mixtures.—Reversal in the Spectrum under various Conditions.—Reversal in Solutions of Oxidizing Substances and other Reversing Agents.

WE have thus far considered photographic processes as originating in the photo-decomposition of the silver haloids without taking into account the particular constituent of the light that produces the chemical change. It is doubtless well known to all that ordinary white light is made up of a number of colours, and it is a familiar fact that such light can be decomposed into its component colours by allowing it to pass through a prism of some dense

transparent substance, such as glass or quartz, or by causing it to be reflected from or transmitted through a surface on which are ruled a number of very fine parallel lines. In the case of a prism the decomposition is produced by refraction and dispersion ; the different coloured rays being unequally refracted, are separated by the dense medium of the prism through which they pass. The violet and blue rays are the most refrangible and the orange and red are the least refrangible, while the green and yellow are refracted to an intermediate extent and thus occupy a position intermediate between the violet and blue on the one side and the orange and red on the other.

The decomposition of light by means of a ruled surface, known technically as a "grating," is due to a process called diffraction. It would take me too far into physical considerations to attempt here to treat of the theories of dispersion and diffraction ; for this portion of the subject I must refer you to works on physics. A few preliminary explanations will suffice to make clear those points which are essential to the complete understanding

of the practical bearing of these familiar facts upon modern photographic processes.

The rainbow-tinted band of colours produced by passing a beam of white light through a prism is known as the spectrum, and it is customary to recognize seven spectral colours, viz. violet, indigo, blue, green, yellow, orange, and red. The spectrum of the intensely glowing carbon points of the electric lamp is now before you on the screen, and you see that it consists of a continuous band in which the colours graduate into each other in the order named. From what has been already said in the way of explanation, it will be understood that the position of any particular colour in the spectrum is a measure of the refrangibility of that colour. It will materially assist us in gaining a more precise idea of the true significance of that spectrum with which we shall have so much to do in the present lecture, if I give a brief sketch of the physical nature of light.

Those among you who have studied physics will know that light is an undulatory movement in a highly elastic medium, known as the ether, which

pervades all space and penetrates between the particles of matter. When the ether is thrown into waves by a sufficiently rapid series of vibrations, the wave-movement is propagated in all directions from the source of the disturbance as a centre with a velocity of about 186,000 miles per second. If the oscillations are below a certain frequency they fail to affect the human eye, but are capable of being detected by appropriate instruments; these longer-period waves are known as radiant heat. On the other hand we may have ethereal undulations which are too rapid to affect the eye; these also can be detected by appropriate methods well known to physicists.

Colour is the visual impression corresponding to oscillation-frequency. If we had a series of ether-waves of one definite rate of oscillation or, what comes to the same thing, one definite wave-length only, we should have a pure monochromatic light of a certain definite refrangibility. White light, as you have seen, is not pure; it is polychromatic, which in physical language means that it is a jumble of ether-waves of different periods and

wave-lengths. When a thin slice of such light is analysed by a prism, the spectrum which we perceive is the result of the sorting out of the waves of different lengths and their classification according to wave-length or oscillation-frequency. The shortest and most refrangible waves produce upon the eye the sensation of violet, while the longer and less refrangible waves produce the impression of red. The actual lengths of the ether-waves are well known to physicists, but all that we need concern ourselves with now is that the wave-length increases from the violet towards the red, while the oscillation-frequency diminishes as we traverse the spectrum in the same direction.[1]

The spectrum formed by a prism possesses certain characters contingent upon its mode of formation which it is desirable to know something about, because it is this kind of spectrum that is most familiar to photographic investigators. It must be borne in mind that the extent occupied

[1] The visible spectrum extends from about the Fraunhofer line A in the red to H in the extreme violet; the wave-length of the A line is 0·0007606 and of the H line 0·0003971 of a millimeter.

by the different colours in such a spectrum does not actually represent the relative proportions of these colours present in the white light; these proportions are necessarily falsified by the prism owing to the unequal refrangibility of the colours. The violet and blue rays being the more refrangible, are separated and spread out to a greater extent than the less refrangible yellow, orange, and red rays. The colours are thus drawn out at the violet end and squeezed up at the red end, so that the space between two points at the more refrangible end separated from each other by any given interval (expressed in wave-lengths) would be greater than the space representing the same interval at the red end of the spectrum.

If we wish to observe the true distribution of colour, we must appeal to the diffraction spectrum, and this is accordingly called the normal spectrum. For most photographic purposes the refraction spectrum answers all requirements, but it is well to remember that it has the defects indicated. Then again you must look upon the extent of the

visible spectrum as a physiological accident depending upon the construction of our eyes, and not as indicating a real physical limit to the ethereal undulations at either end of the band of visible colours. Both beyond the violet and below the red there are ether-waves incapable of affecting human vision; the infra-red waves, as I have already said, may be regarded as radiant heat, and the ultra-violet rays can be made visible by allowing them to fall upon certain substances which alter their wave-length in such a way as to bring them within our visual capacity. Substances which possess this property of changing the wave-length of an ethereal undulation are said to be *fluorescent* [A]. These ultra-violet waves have no special designation, simply because we have no specialized organ of sense for perceiving them, but we shall soon learn that from a photographic point of view they are of the highest importance.

In considering instances of photo-decomposition it is essential that we should know something more definite than that a compound is simply decomposed by light. If our knowledge is to be com-

plete we should know what particular constituent of the light is most effective in causing decomposition. Looking at the visible spectrum of white light, such as that of the electric light which is now on the screen, the first thing that strikes us is that the maximum of visual intensity is in the yellow. The first and most obvious question that arises is whether that colour which appears the most intense to the eye is the most active in promoting photo-decomposition—is visual intensity the same as photographic intensity? The earliest experiments made in this direction take us back to the year 1777, when Scheele allowed the solar spectrum to fall on a sheet of paper coated with silver chloride, and thus found that the salt darkened most rapidly in the violet rays. This fundamental experiment can be easily repeated by throwing our electric light spectrum on to a sheet of silver chloride paper [B]. You see the violet end has become perceptibly discoloured, while the strongly luminous yellow has not produced any visible effect—photographic intensity does not coincide with visual intensity.

The line of investigation opened up by Scheele has been followed by numerous chemists and physicists, among whom I need only mention the names of Herschel, Becquerel, J. W. Draper, Fox Talbot, and Robert Hunt, to convince you that the problem has been regarded as one of no inconsiderable importance. In more recent times every photographic investigator who has concerned himself with the scientific development of the subject has felt it necessary to study the action of the spectrum upon the silver haloids or other photo-sensitive compounds. As the final outcome of all the work which has hitherto been done, it may be taken as fully established that visual intensity and photochemical activity are in no way related. The fact that yellow and orange appear brighter to us than violet and blue is another physiological accident. In the majority of compounds known to be photo-sensitive, it happens that the violet end of the spectrum is the most effective in promoting decomposition. Could we look upon nature with a photographic eye, we should experience some strange reversals of colour impression ; a wood in

springtime carpeted with violets and wild hyacinths, for instance, would appear a more brilliant spectacle than a meadow ablaze with golden buttercups.

That the violet and even the ultra-violet rays are the most effective in the majority of cases is a fact that is true not only for the silver haloids, but also for the ferric, uranic, cupric, and mercuric salts, for the chromates, and for the salts of gold and platinum. In view of this circumstance it is not surprising that the more refrangible end should have been formerly regarded as the region of special chemical force. In the older works on physics we find the spectrum divided into the three regions of heat, light, and actinism or chemical force. With the advancement of knowledge this division has broken down; the notion that a chemical force resided in the violet rays was due simply to the circumstance that the most familiar compounds, and especially the salts of silver, were more sensitive to these rays. It is now well known that many substances are sensitive to the less refrangible radiations, and even the silver haloids

themselves can, as we shall see presently, have their sensitiveness so modified as to be decomposed by the red end of the spectrum.

The importance of knowing the specific action of the spectral colours on the silver haloids may not be apparent at first sight. If you consider, however, that the various objects focussed on the camera screen in order to be subsequently photographed are possessed of different colours, the necessity for this knowledge will become obvious. It will be readily understood that objects will impress themselves upon an ordinary photographic plate with an intensity proportional to the amount of violet and ultra-violet light which enters into the composition of the colour which they reflect or scatter. The fact that reds and yellows impress themselves feebly, while violets and blues impress themselves strongly, is one of the most familiar experiences of the practical photographer. So also the varying photographic activity manifested on different days according to the state of the atmosphere, the height of the sun above the horizon, &c., is well known to all workers with the

camera. The different exposures necessary on different occasions represent the varying amounts of blue, violet, and ultra-violet rays, absorbed from the sun's light by our own atmosphere under its different conditions of humidity, or according to the amount of suspended matter which it contains. It can easily be understood also that the length of atmosphere traversed by the solar rays depends upon the altitude of the sun above the horizon, and this is why the photographic efficiency of daylight is greater at noon than earlier or later in the day.

From the photographer's point of view it is an extremely fortunate circumstance that the colours of natural objects are never pure. By this I mean to say that no colour would appear perfectly monochromatic if we analysed its light and observed its spectrum. The colour of any natural object is always a mixture—some rays of the spectrum are absorbed and others are reflected, so that the colour which finally reaches the eye is a residual effect. In addition to this a certain amount of white light is scattered from all surfaces except

dead black. Were it not for the latter circumstance, a photographic picture would present much more violent contrasts of light and shade than we actually witness.

The composite character of a colour which appears simple to the eye can be well shown by means of certain artificial colouring matters. The light transmitted through a glass cell containing a solution of "aniline blue" appears on the screen of a rich blue colour, and this solution of "iodine green" apparently transmits nothing but green. On analysing these colours by passing them through a prism you see that red is present in both cases, a fact which the eye utterly fails to perceive before the prismatic analysis [C].

It will be evident from the explanations which have now been given that the position of any colour in the spectrum is due to the length of the corresponding ether-wave, so that we have a true physical measurement of colour independent of its subjective sensation. For photographic purposes it is necessary to have some recognized positions of reference—some definite lines in the

spectrum which we can talk about instead of mentioning the colours by name. Such fixed lines are found in the spectrum of sunlight and are generally used for this purpose. The lines in the solar spectrum to which I allude are narrow dark lines traversing the spectrum at irregular intervals in a direction perpendicular to its length; they are known as the Fraunhofer lines, after the physicist who first accurately mapped them. It is no part of the present subject to explain here the origin of these dark lines; it will suffice to state that they are produced by the absorption of the particular waves which they represent in position by gaseous and vaporous substances in the sun's, as well as in our own atmosphere. The more important of these dark lines, which you see in the photograph of the solar spectrum thrown on the screen, furnish the necessary positions of reference.

In order to study practically the photo-reducibility of the silver haloids or other compounds by different colours of the spectrum, the older experimenters often made use of coloured glasses; but

this method is obviously unsatisfactory because the light transmitted by such media is seldom monochromatic [D]. A far more scientific mode of procedure is to photograph the spectrum itself, a narrow slice of white light being allowed to pass through a prism, and the spectrum being then focussed on the photographic surface to be examined. The source of light may be the sun, the electric or oxyhydrogen light, burning magnesium, or any other source of radiation rich in rays of all refrangibilities. It is important to remember in carrying out such experiments that the materials composing the lenses and prisms of the spectrographic apparatus have a certain specific absorbing power. It is well known, for instance, that glass absorbs more or less of the ultra-violet light, so that in very exact work we must either use a diffraction spectrum or have our lenses and prisms of quartz, as first pointed out by Prof. Stokes in his classical researches on fluorescence.

When a spectrum is allowed to fall on a photographic surface, the amount of decomposition induced in the different regions is shown by the

degree of darkening of the silver compound, or, instead of allowing the spectrum to act till visible discoloration is produced, a short exposure may be given and the invisible impression developed in the usual way. Both these methods have been employed by different experimenters. The results may be expressed by a graphical method which is now so generally adopted that we must understand its principle before making further progress.

Supposing, for example, we wished to show the visual intensity of the spectral colours by means of a curve. We may take as ordinates a series of lines drawn perpendicular to the spectrum, the height of these lines being made proportional to the intensity of the colours as seen by the eye, or, more accurately, as measured photometrically.[1] For practical purposes the strongest of the Fraunhofer lines answer all requirements. The intensity of the colour seen at the position corresponding to each of the selected lines would be marked off as a point on each line, and the points then joined by a

[1] See Abney and Festing's Bakerian Lecture for 1886. *Phil. Trans.* Part II. 1886, p. 423.

curve which would show at a glance the distribution of visual intensity in the spectrum. The result is shown in the diagram :—

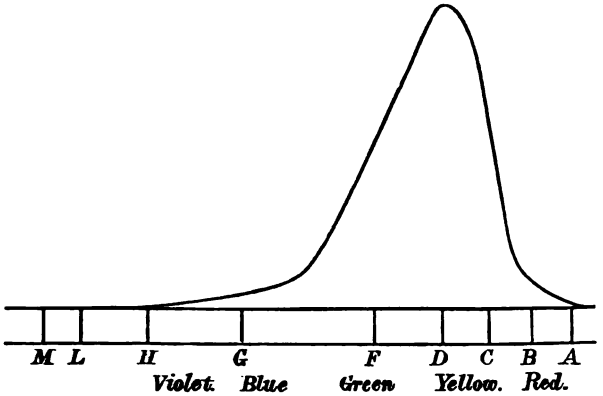


FIG. 5.—VISUAL INTENSITY OF COLOURS OF SOLAR SPECTRUM.

From such a diagram it is at once seen that the maximum of visual intensity is in the yellow, a little to the more refrangible side of the line *D*. It is seen also that the visible spectrum extends from near the line *A* in the red to about *H* in the extreme violet. In a similar way the distribution of heat might be represented by another curve, the maximum of which would in this case be in the infra-red. The same method is applicable to the representation

of photographic intensity. The amount of decomposition undergone by a silver haloid in different parts of the spectrum is shown by the degree of darkening on long exposure, or by the density of the silver deposit with short exposure and development. It is only necessary to make the lengths of the ordinates (Fraunhofer lines) proportional to the degree of darkening, and then connect the abscissæ by a curve as before. The curve then shows at a glance the distribution of photochemical efficiency in every part of the spectrum for the particular salt employed.

We are now, I venture to think, in a position to follow the results of recent work in spectrum photography. The action of the pure spectrum upon the silver haloids in various conditions and in different vehicles has been studied by many investigators, especially by J. W. Draper, Hunt, Herschel, and Becquerel, and most recently by Abney with improved appliances, and with greater care in eliminating the effects of impurities than has hitherto been bestowed upon this branch of work. I shall of course be unable to

do more than give you a general notion of the results obtained. The first question to be asked is whether the different haloids have the same maxima of sensitiveness, and this can be answered by experiment in a somewhat rough and ready way by allowing our spectrum to fall on three slips of paper coated with the respective haloids and, after a sufficient exposure, developing in the usual way [E]. The result shows that with the chloride the maximum is in the violet, just about or a little beyond the limit of the visible spectrum; with the bromide the maximum is in the blue, and with the iodide also in the blue, but a trifle more towards the violet end. You will notice also that the bromide spectrum is longer than either of the others—that it extends more towards the red, a fact of which we shall see the practical significance hereafter.

The experiment shown is necessarily a hasty one, and gives only a crude idea of the local action of the spectrum upon the different haloids. In more exact work the greatest precautions have to be taken to insure trustworthy results

—the effect due to every substance associated with the haloid, whether as an essential constituent of the film, or as an accidental impurity, must be studied individually before we arrive at the true photographic spectrum of the haloid. It is no doubt the neglect of these precautions which has led former workers to give different positions to the maxima of decomposition for the same haloid. The action of impurities makes itself especially felt with prolonged exposure, so that the spectrum printed up to the stage of visibility is never so satisfactory as that formed by a short exposure and subsequent development. The final result of all the recent experiments is summed up in the following diagram :—

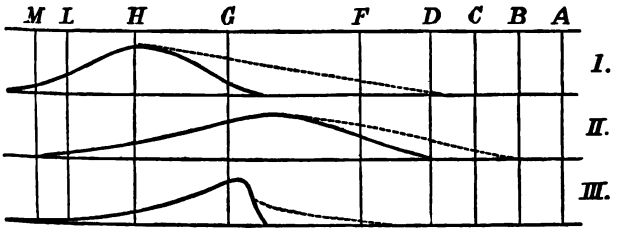


FIG. 6.—SPECTRUM PHOTOGRAPHED ON THE SILVER HALOIDS.

I. Chloride; II. Bromide; III. Iodide. The dotted curves show the extension towards the red by longer exposure.

The chief point of interest in connection with these curves is that they represent a physical reality—they indicate a fundamental property of the silver haloid molecule. What that property is we shall learn subsequently. The curves show that each haloid is most susceptible in one particular region of the spectrum. The cause resides in the molecule itself, and is inherent in that molecule. We cannot shift the maximum of any of these curves; by careful experiments with the pure haloids the maxima are always in the same position. The same curves are obtained, when the necessary precautions are observed, by direct printing or by development; the state of molecular aggregation of the haloid makes no difference; neither does the vehicle nor the sensitizer, provided these do not form actual chemical compounds with each other or with the silver haloid. The length of the photographed spectrum may be increased by longer exposure or by other methods—we may encroach more and more into the red, or we may even so modify the haloid as to get a new maximum

in the less refrangible region, but the position of the maximum in the blue or violet is not thereby affected.

Interpreting these results practically we see that silver chloride has the advantage for light which is rich in violet and ultra-violet rays, while the bromide and iodide have the advantage for blue rays. It is not to be understood that these photographed spectra give us any measure of absolute sensitiveness, because, as you are now aware from former lectures, this is influenced also by many other conditions. But when white light or the rays from a coloured object fall on a sensitive plate, it is evident that that haloid which is acted upon by the greatest range of spectral colours must have the advantage in the way of sensitiveness. You will understand this if you consider that the image thrown by a lens sums up on the surface of the film all the rays emitted by the object whose image it forms.[1] A haloid which is affected by the violet, blue,

[1] Excepting the small percentage absorbed by the material of the lens.

green, and yellow rays during the same exposure which in the case of another haloid would allow only the violet rays to act, must offer advantages in the way of sensitiveness. You have seen that with the same exposure silver bromide gives a longer spectrum than the other haloids; that means that this haloid is more sensitive for green, yellow, and red than the chloride or iodide, and there is no doubt that this property is one of the many causes which combine to make silver bromide so highly sensitive in modern photographic processes.

The next point to be considered is the action of the spectrum upon mixtures of the haloids. If there is an excess of some good sensitizer present capable of rapidly absorbing the liberated halogens, the maximum due to each spectrum is impressed—the photographed spectrum is a resultant due to the compounding of the spectra of the separate haloids. But if the above condition is not fulfilled, *i.e.*, if there is not an efficient sensitizer present, a very different effect is observed. This effect, whatever may be its

true explanation, is a very remarkable one, and we are indebted for its discovery to Capt. Abney, who has worked out the essential conditions by a most laborious series of experiments. I can do nothing more now than give a very brief summary of the conclusions of this investigator.[1] The general nature of these results will be best seen from the following curves,[2] selected as types

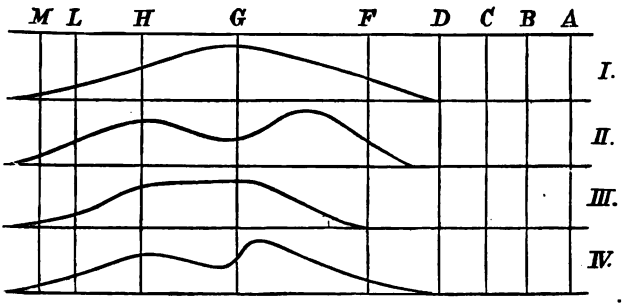


FIG. 7.—CONCURRENT REVERSALS IN MIXTURES OF SILVER HALOIDS.

from a large number published by Abney in illustration of his work.

Let me first explain the meaning of each

[1] See chap. xxxv. of his *Treatise on Photography*, 5th ed. p. 277; also *Proc. Roy. Soc.* vol. xxxiii. p. 164.

[2] I am indebted to Capt. Abney for permission to reproduce the curves shown in this and other figures.

curve before attempting to interpret the principle which they reveal. The four spectra have been selected so as to be fairly comparable in two pairs. Thus I. and II. represent the action upon mixtures of bromide and iodide in collodion. In I. a wet plate sensitized with silver nitrate was used, and the image developed by an acid or alkaline developer. In II. the conditions were precisely the same, excepting that the excess of silver nitrate was washed out. In III. there was a mixture of iodide and chloride on paper sensitized with silver nitrate, the image being developed after a short exposure as before. In IV. the same haloids were used in gelatine, no other sensitizer being present, and the image was developed as before. Now compare the results:—

The only difference between I. and II. is that in the former there is a sensitizer ($AgNO_3$) present, while in the latter there is nothing but a mixture of bromide and iodide with practically no sensitizer. You see that in curve I., as might have been expected, we have the superposed

spectra of the bromide and iodide with their common maximum about G. But in II. there is a totally different state of affairs—the common maximum near G has become a minimum, and there are now two maxima, a minor one near H, and another in the blue-green between G and F. The same difference exists between III. and IV. When $AgNO_3$ is present, the curve is compounded of the chloride and iodide curves; when the sensitizer is absent—for gelatine is such a comparatively feeble sensitizer that its action may be neglected in this case—we have as before a minimum about G, a maximum in the blue-green (rather nearer the blue than in II.), and another minor maximum in the violet, near H. Reduced to practical terms these facts simply mean that in the absence of sensitizers a mixture of haloids is more sensitive to the blue-green, and less sensitive to the violet rays of the spectrum than either haloid separately.

We have next to consider how these results may be interpreted. The case of a mixture of haloids with excess of sensitizer is quite normal

and requires no special explanation; the remarkable destruction of sensitiveness about G and the shifting of the maximum into the blue-green when the sensitizer is absent, are the chief facts requiring comment. The most obvious explanation would at first sight appear to be that about G there is a reversing process going on, owing to the rehalogenization of the sensitizer, in accordance with the principles discussed in the last lecture. This explanation is, however, rejected by Abney, for the very good reason that the effect is not analogous to ordinary solarisation, because the same result is obtained even with a very short exposure. But although ordinary reversal is inadmissible under these circumstances, it is not improbable that we have to do with an analogous phenomenon due to the same chemical cause.

In order not to complicate the argument it will be well to restrict attention to one pair of haloids only, say the bromide and iodide. The region of the spectrum where the greatest amount of decomposition goes on is about G; it is here that the greatest amount of bromine and iodine would be

liberated in a given time. If the removal of the halogens keeps pace with their liberation, as is the case in the presence of a sensitizer, the largest amount of reduction product is formed in this region—we have the maximum of intensity on development as appears in curve I. But if the halogens are not speedily removed—if no active sensitizer is present, their rapid accumulation must more or less undo the work done by the blue rays; not only because of the actual quantity of these halogens as compared with the amount of reduction product, but also because of the fact that bromine and iodine when liberated simultaneously would form a compound, a bromide of iodine, which would probably be more active as a rehalogenizer than halogen alone. Chemists have long been familiar with the fact that a mixture of halogens is often more effective in chemical reactions than the halogens by themselves.

So far then the explanation is perfectly straightforward, and it will be seen that the process is similar to that which occurs when the latent image is destroyed by a halogen, only the latter

is supplied (and probably in a more active form) by the haloid in the film itself instead of from an external source. The effect is thus analogous to ordinary reversal with the part played by the halogenized sensitizer left out. The element of time does not come in because the rehalogenization goes on with the action of light *ab initio:* the reduction of sensitiveness about G may be attributed to what I will venture to call *concurrent reversal.*

The increase of sensitiveness in the green is attributed by Abney to the formation of a new molecule, a bromo-iodide of silver of the formula AgBr,AgI, or Ag_2BrI. This compound is supposed to be formed by the action of the bromine liberated from the bromide upon the iodide, the latter being almost insensitive in this part of the spectrum, while the bromide is acted upon by this colour, as will be seen by comparing curves II. and III. of Fig. 6. The bromo-iodide thus formed is believed to be more sensitive for the green, and in support of this view it has been found that if a surface of washed silver bromide is darkened by exposure to light and then brushed over with a

solution of iodine, a compound is obtained which behaves towards the spectrum in precisely the same way as the mixture. The conclusions drawn from these facts are perfectly sound, but chemists are not very willing to admit the existence of new molecules without adequate proof. I will remind you therefore that there is a rare bromo-iodide of silver said to occur as a native mineral in Chili, and there are a whole series of chloro-bromides containing various proportions of metal, chlorine, and bromine, of which the Chilian mineral embolite, Ag_3BrCl_2, is perhaps the best known. But the most conclusive proof is furnished by Abney's experiments with surfaces of silver bromide or chloride, darkened by exposure to light, rehalogenized by iodine, and then exposed to the spectrum *in the presence of sensitizers.* Under these circumstances curves similar to IV., Fig. 7, are obtained [F]. The point of this illustration is that the sensitiveness to blue-green is shown even in the presence of a sensitizer; if the silver haloids were present as a mere mixture, you know that under these circumstances we

should have had a resultant spectrum as in curves I. and III.

With respect to the chemistry of this last experiment it is difficult to offer any suggestions which are not more or less speculative, owing to our ignorance of the true composition of the reduction product. But it may be useful to consider what might happen on the supposition that this product is an oxyhaloid. It is pretty certain that the old sub-haloid formula will have to be abandoned, and the sooner we familiarize ourselves with other possible ways of regarding these reactions, the better will it be for future progress. Thus, if we suppose that the compound formed by the action of light upon silver bromide is the oxybromide, Ag_4OBr_2, the destruction of this product by iodine in alcoholic solution might be represented by the equation :—

$$Ag_4OBr_2 + I_2 + C_2H_6O = 2Ag_2BrI + C_2H_4O + H_2O$$

In the absence of alcohol the oxygen of course meets a different fate—it may escape in the free

state or it may form oxidized products with some of the iodine. The bromo-iodide may give as a reduction product a mixed oxyhaloid, Ag_4OBrI. Such are the possible processes which may go on when the spectrum falls on a mixture of the bromide and iodide, the iodine which rehalogenizes the oxybromide being in this case supplied by the decomposition of the silver iodide by the liberated bromine.

From the action of the spectrum upon the silver haloids with short exposure, it is only a natural step to the action of the spectrum with prolonged exposure: if the exposure is long enough to produce reversal, in what part of the spectrum does this phenomenon occur? Two of Abney's curves, shown in the accompanying diagram (p. 268), will answer this question for silver iodide and for a mixture of bromide and iodide.

In No. I. pure silver iodide was sensitized by silver nitrate and developed after long exposure: in No. II. a mixture of three molecules of the iodide and one molecule of the bromide was exposed in the presence of excess of silver nitrate (wet

collodion plate), and then developed by the acid or alkaline method. Both these curves point to the fact that the region of reversal is at the ordinary maximum of decomposition near G. The iodide curve is particularly instructive: in the position where the curve shows a maximum with short exposure, there is now a depression, thus making it appear as though a new maximum

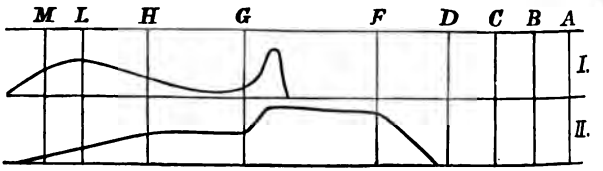


FIG. 8.—ORDINARY REVERSAL IN SPECTRUM.
I. Pure AgI + $AgNO_3$; II. 3AgI + AgBr + $AgNO_3$.

nearer the green had been produced. It is evident, however, that this shifting of the maximum is only apparent; the true maximum is reversed, and the elevation on the less refrangible side simply represents a small residue of unreversed reduction product. From the theory of solarisation which was discussed in the last lecture, it is obvious that these curves express results which might almost

have been anticipated: where the evolution of halogen is most rapid, rehalogenization (reversal) might be expected to occur the soonest. It may be regarded as a general rule that when a silver haloid is given a very prolonged exposure to the spectrum in the presence of a sensitizer, *reversal begins in that region where the decomposition reaches a maximum with a short exposure.*

We may now pass on to the consideration of the action of the spectrum upon the silver haloids in the presence of true reversing agents and other substances, both oxidizing and reducing. This subject will be best approached by returning for a short time to purely photochemical actions. It will be remembered that it was stated at the very beginning of our subject that light in some cases promotes oxidation (Lecture I., p. 25). We are now in a better position to deal with this property of light, and I will commence by putting you in possession of some well-known facts.

Although in most instances of photochemical reduction, the violet and blue rays are the most

effective, it appears that in many cases where oxidation is accelerated by light the red rays are the most active. Thus the photo-oxidation of lead compounds, of mercurous oxide, of ferrous and manganous compounds, of arsenites and of sulphides, proceeds more rapidly in the red than in the violet rays. It must not be understood that I am now laying down a general law, because we know of many instances of photo-oxidation by the more refrangible rays, and, on the other hand, we shall learn subsequently that the red rays may be made to bring about photo-reduction of the silver salts. But we must fully prepare ourselves for the possibility of photo-oxidation ; we must learn to look upon a photo-sensitive surface as the seat of chemical changes in which both reduction and oxidation may be taking place simultaneously, the final result being determined by the relative rates at which the two processes go on. This amounts to the same thing as saying that the final product of photo-decomposition is determined by the nature of the compound with which the

photo-sensitive substance is associated, as well as by the nature of this last substance. Starting from these general notions we may next proceed to consider some concrete instances.

In the last lecture the reversing action of potassium iodide upon darkened silver chloride was shown. It will be remembered that a sheet of paper coated with the haloid was darkened by exposure to light, and then bleached by a further exposure when painted with a solution of potassium iodide. The rehalogenizing action of the soluble iodide was explained as being the result of the oxidation of this salt by atmospheric oxygen. By repeating the experiment in the spectrum we shall find out which constituent of the light is the most active in this reversing process [G]. The result shows that the bleaching action takes place in the same region of the spectrum where the maximum of decomposition occurs in the absence of a reversing agent. The action cannot be the same as in ordinary solarisation, because the silver chloride has already lost its removable chlorine

by preliminary exposure: the potassium iodide may indeed be looked upon as playing the part of the halogenized sensitizer, but the co-operation of oxygen is a necessary condition of its bleaching action under the conditions of the experiment. The result is a good illustration of the principle from which we set out: the photo-sensitive compound is here potassium iodide, the photographic surface is the reduction product of silver chloride. It happens that potassium iodide is one of those compounds which undergo oxidation most rapidly in the blue and violet rays; hence the bleaching action is strongest at the most refrangible end of the spectrum.

Investigations in the direction indicated by the last experiment have been made by Abney with glass plates coated with the silver haloids in different vehicles. The plate is first given a preliminary exposure, then immersed in a glass cell containing the solution or gas to be tested, and exposed to the action of the spectrum and developed. The results obtained are of extreme

interest and some of the curves are shown in the diagram on p. 274. It must be borne in mind that a curve above the line indicates normal action, while a curve below the line signifies reversal, the local intensity of the reversal being indicated as before by the height of the curve at different points.

It is by no means easy in the present state of knowledge to see the precise meaning of these curves, and we must be satisfied if we can get but a glimpse into the photochemical processes which they reveal. No. I. represents what may be called normal reversal in an ordinary gelatino-bromide plate given a prolonged exposure to the spectrum, and about this there is not much mystery. You know that silver bromide is sensitive as far as the red if it only gets exposure enough; the curve which has its maximum near G creeps gradually towards the red as the spectrum continues to act (Fig. 6, II.). This curve No. I. simply shows therefore that while halogenization of the sensitizer (gelatine) is going on very rapidly at the blue end, it is going on

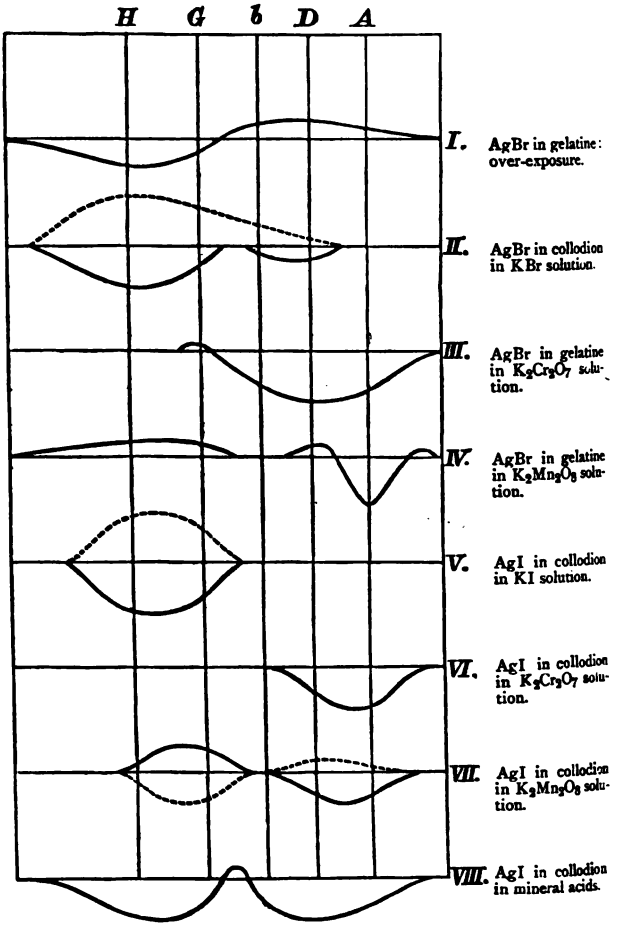

H
G
b
D
A
I. AgBr in gelatine: over-exposure.
II. AgBr in collodion in KBr solution.
III. AgBr in gelatine in $K_2Cr_2O_7$ solution.
IV. AgBr in gelatine in $K_2Mn_2O_8$ solution.
V. AgI in collodion in KI solution.
VI. AgI in collodion in $K_2Cr_2O_7$ solution.
VII. AgI in collodion in $K_2Mn_2O_8$ solution.
VIII. AgI in collodion in mineral acids.

FIG. 9.—REVERSALS IN SPECTRUM IN PRESENCE OF REVERSING AGENTS.

more slowly at the red end, so that by the time the blue end has received enough bromine to constitute what I will call a reversing charge, the red end has only received enough to produce a normal impression on development.

Such curves as II. and VIII., which show two maxima, are the most difficult to explain satisfactorily, but it is worth while to make an attempt to unravel their meaning, if only to get suggestions on which to base further experiments. The first of these was obtained by giving a collodio-bromide plate a preliminary exposure to diffuse white light, then immersing in a five per cent. solution of potassium bromide (acidified), exposing to the spectrum and developing. No. VIII. represents the action of the spectrum upon a collodio-iodide plate (after preliminary exposure) when immersed in a mineral acid. It may be added that collodio-iodide when immersed in a solution of potassium bromide gives a curve somewhat similar to No. II., only the minimum of reversal is at *b*, and the second maximum is shifted more into the red. The curve showing the action of

the spectrum on a silver bromide film in mineral acids is similar to No. VIII., but the region of least reversal is between *b* and D instead of between G and *b*.

In attempting to understand these results it is essential to bear in mind the complexity of the conditions under which the experiments are made. We start with a film which has had a preliminary exposure and therefore containing a mixture of unaltered haloid and reduction product, together with partially halogenized sensitizer. This is immersed in the solution and the spectrum allowed to act upon it. The conditions are favourable to reversal because the silver haloid is already partially dehalogenized. When therefore the spectrum falls upon this surface, the rays which are most active in decomposing the substance dissolved in the solution will produce the maximum reversal; the maxima at the blue end, in curves II., V. and VIII., are thus due to a similar action to that which occurs when the spectrum is allowed to fall on a sheet of darkened silver chloride paper coated with

potassium iodide. These blue end maxima are in fact the curves of normal action reversed, the dotted curves above the line in II. and V. showing the positions of the ordinary maxima of decomposition.

The reversals at the red end of the spectrum are more difficult to deal with. There is no doubt that these represent the chemical destruction of the reduction product by oxidation, since oxidizing solutions are most favourable to their production. In fact it has been found that in reducing solutions, such as potassium nitrite, sodium sulphite, or pyrogallol, no reversal at all takes place. Reversals in potassium dichromate and potassium permanganate are shown in curves III., IV., VI., and VII. A collodio-iodide plate in hydroxyl gives a curve very similar to VII. It must be understood that all these curves are produced in the same way, viz. by preliminary exposure of the plate, then immersion in the solution and exposure to the spectrum. The general effect of oxidizing agents is to enormously increase the rate of reversal by the less refrangible rays. Thus in

IV. and VII. it is seen that the result is a mixed one—the action is normal at the violet end and reversed at the red end. This means that in the latter region the destruction of the reduction product has been going on to a great extent by photo-oxidation, while at the violet end the haloid was still undergoing photo-reduction: in other words, reduction and oxidation have been going on simultaneously at the two ends of the spectrum. Potassium dichromate causes reversal only at the red end as seen in III. and VI. It is probable that the specific absorption of the salt has something to do with this limitation of action, because it cuts off the violet and blue end of the spectrum. This appears from a comparison of the dichromate curves with those given by permanganate, *i.e.* III. with IV. and VI. with VII. Potassium permanganate exerts strong absorption in the green, but transmits the violet and blue rays at one end and the orange and red at the other end. The dichromate thus agrees with the permanganate in its action upon the less

refrangible rays, but acts as a screen towards the more refrangible rays: for this reason we get no action in the blue with the former salt, while we have a distinct image in this region with the permanganate [H].

Now although the absence of all action in the violet and blue, either direct or reversed, in the case of dichromate is intelligible in the light of the explanation which has just been offered, there is an apparent mystery about the proceedings at this end of the spectrum when we have to do with potassium permanganate which requires clearing up. I allude to the fact that the violet and blue rays which are transmitted by this solution produce only a direct or normal impression with the same exposure which produces distinct reversal in the red. This appears all the more remarkable when we consider that these very same rays when transmitted through colourless solutions, such as potassium bromide (No. II.), potassium iodide (No. V.) and mineral acids (No. VIII.), cause strong reversal. It is possible that the rays in question are

absorbed to some extent by passing through the permanganate and their chemical activity thus deadened. But I do not think that this is the true explanation of the phenomenon. It seems more likely that we have here a case of *retarded action* in the violet and blue owing to the presence of the oxidizing salt. It has been amply proved in former lectures that substances which tend to prevent the liberation of halogen retard the photo-decomposition of the silver haloids. The action of the permanganate would thus be to retard the formation of reduction product in that very region where in the absence of this salt the photo-decomposition would proceed most briskly, while at the red end there would be going on photo-oxidation of the reduction product already formed by preliminary exposure and subsequently. The final result would be that by the time a distinct normal image had been formed by the violet and blue rays, a strong reversed image would be produced by the red rays (Curves IV. and VII.). In accordance with this explanation I will remind you that an

oxidizing substance like hydroxyl, *which is perfectly colourless*, gives a very similar curve to VII. Here also we must look upon the result as due to retarded reduction at the violet end and photo-oxidation at the red end. If the permanganate solution is very dilute, both retarding and oxidizing action are so enfeebled that normal reversal occurs, as shown by the dotted curve in VII.

We might thus go on discussing these and many more such curves and learn something from each one of them. But you have probably seen sufficient by this time to enable you to understand how these results may be dealt with in a general way. The remarkable curve (No. VIII.) produced by the action of mineral acids almost tempts me to digress further, but I will content myself by pointing out that these acids, not being oxidizing agents (except nitric acid), do not exert that retarding action in the violet and blue, and this may explain why we get the two maxima of reversal so strongly developed. The strong reversing action of potassium bromide

shown in curve II. explains why all excess of this salt must be washed out of a gelatine emulsion in order to insure the condition of greatest sensitiveness (see Lecture IV., p. 123).

With regard to the chemical actions concerned in these reversals it is important to remember that there is a great distinction between the action of white light and the action of the spectrum as a reversing agent. White light gives us the final result of a number of operations some of which tend to undo the work of others—we have an end result which may be regarded as the *algebraical sum* of all the chemical actions going on. In the spectrum these effects are differentiated and each set of rays produces its own particular action, so that the photo-reduction taking place in one region is not complicated by concurrent photo-oxidation at the same place. Thus in such solutions as potassium permanganate and hydroxyl, which transmit the violet and blue, these rays can exert their reducing action unchecked except

by the retarding action of the oxidizing substances upon the silver haloid. This is also another reason why in these solutions we get no normal reversal at the more refrangible end. In the red rays the photo-oxidation proceeds without check from concurrent reduction, and thus gives rise to the strong reversal shown in the curves. The destruction of the reduction product in the spectrum is thus a simpler phenomenon than the same process in white light. From the circumstances that these experiments have been made upon plates immersed completely in the solutions, it would appear that atmospheric oxygen does not play such an important part in these reversals in the spectrum, even in the case of reversing substances like the alkaline haloids or the haloid hydracids which are not oxidizing agents under ordinary circumstances. We must in fact admit the possibility of direct interaction between the reduction product and these reversing agents under the influence of particular rays. Adopting the oxyhaloid formula we may expect such reactions as those typified by the equations:—

$$Ag_4OBr_2 + 2HBr = 4AgBr + H_2O$$
$$Ag_4OBr_2 + 2HI = 2AgBr + 2AgI + H_2O$$
$$Ag_4OI_2 + 2KI + H_2O = 4AgI + 2KOH$$
$$Ag_4OBr_2 + 2KI + H_2O = 2AgBr + 2AgI + 2KOH$$

In the case of direct oxidation by ozone or by such salts as the dichromates and permanganates, the destruction of the reduction product may be due to indirect rehalogenization by the oxidation of the halogenized sensitizer as explained in the last lecture, or it may be represented as a direct action of oxidation:—

$$2Ag_4OBr_2 + 2O_3 = 4Ag_2O + 2Br_2 + 2O_2 \text{ (first stage).}$$
$$2Ag_2O + 2Br_2 = 4AgBr + O_2 \text{ (second stage).}$$

The nature of the substance with which the silver haloid is associated must evidently determine the particular mode of destruction of the oxyhaloid.

APPENDIX TO LECTURE VII.

A (p. 242).—Shown by the usual method of placing a card painted with sulphate of quinine in the violet and ultra-violet region of the spectrum of the electric light. If a quartz prism is not available flint-glass must be used in order to get the best effect.

B (p. 243).—A sheet of paper coated with silver chloride and sensitized with silver nitrate is placed in the spectrum of the electric light as described in the text. During exposure the limits of the different colours of the spectrum are marked out by pencil lines just below the spectrum seen on the paper. When the exposure has been sufficiently long to produce visible discoloration, the paper is withdrawn. It is then seen at once by the pencilled lines which region of the spectrum has produced the greatest effect.

C (p. 248).—The solutions of the colouring matters are placed in flat glass cells with parallel sides and interposed between the slit in the lantern

nozzle and the prism. The aniline blue is the "soluble blue" of commerce dissolved in water and acidified with a few drops of dilute sulphuric acid. Instead of iodine green, "malachite green," or almost any of the coal-tar greens can be used, as they all transmit a band in the red. The exact strengths of the solutions must be previously found by trial.

D (p. 250).—The absorption-spectra of various coloured glasses were thrown on the screen by interposing the media between the slit and the prism in the usual way.

E (p. 254).—The papers are prepared in the ordinary way, care being taken to remove excess of silver nitrate by a final immersion in a solution of the corresponding alkaline haloid. Three long and narrow strips are cut, washed with water till free from soluble salts, and then sensitized with a solution of sodium nitrite or sulphite. The three strips are fastened on a board and exposed for one or two minutes, the total width and length of the sensitive papers being sufficient to be covered completely by the spectrum. The strips are washed and developed by ferrous oxalate. The distribution of colour is shown (as in Experiment B.) by pencil lines drawn beneath the spectrum during exposure.

F (p. 265).—Paper coated with silver bromide is

exposed to the electric light till darkened, then brushed over with a weak alcoholic solution of iodine, washed with water, sensitized by sodium nitrite, exposed to the spectrum for one or two minutes, then washed and developed by ferrous oxalate. The spectrum colours are pencilled out as before; a maximum appears in the green on development.

G (p. 271).—Paper coated with silver chloride is darkened by exposure to white light, then brushed over with a solution of potassium iodide and exposed to the action of the spectrum (See Experiment I., Lecture VI., p. 233). The experiment can be repeated with silver bromide, giving a short exposure and developing with ferrous oxalate.

H (p. 279).—The absorption-spectra of solutions of $K_2Cr_2O_7$ and $K_2Mn_2O_8$ are shown on the screen in the usual way.

LECTURE VIII.

Relationship between Photochemical Decomposition and Absorption of Light.—Draper's Law.—Effect of Molecular Aggregation upon Sensitiveness of Silver Haloids.—Photography of Red and Infra-Red Rays.—Physical Analogy between Emission Spectra and Photographed Spectra.—Photochemical Action probably intramolecular.—Effects of Dyes on Local Sensitiveness.—Orthochromatic Photography.—Photochromy.

IN the present lecture we must set out from certain fundamental physical conceptions. If a chemical compound absorbs some of the rays of the spectrum, the energy of the ethereal undulations producing those rays must be used up in doing some kind of work upon or within the molecules of the compound. There may be a production of heat or of electricity, or there may be chemical decomposition, an equivalent quantity of the absorbed light dis-

appearing as such. These statements will be self-evident to those who are familiar with the teachings of modern physics — they are based upon the universally received doctrine of the conservation of energy. At the present moment it is with photo-chemical decomposition that we are alone concerned.

The inherent property of the molecule of a silver haloid which confers upon it its sensitiveness to special rays is its power of absorbing those rays. This faculty is no doubt ultimately dependent upon the mechanical structure of the molecule, but it is beyond my province to deal here with these questions of molecular physics. The proof of this statement does not rest however upon such *à priori* mechanical conceptions, but is capable of experimental demonstration. It has been shown by many experimenters that whenever a beam of light passes through a sufficient thickness of a solution or gas in which photochemical change is induced, the emergent light is deprived of the faculty of producing any change in a further quantity of the same solution or gas. The special

undulations which are effective for the particular substance are sifted out of the beam, and the residual rays are thus wanting in that constituent which is capable of affecting the substance being experimented with. This has been proved in the case of solutions of ferric and mercuric salts in the presence of reducing agents as well as for other mixtures [A]. It may thus be taken as a general law that photochemical decomposition implies the absorption of some particular constituent of the light, and as this was first distinctly enunciated in 1841 by the American physicist J. W. Draper, it will be well to associate the principle with its discoverer and to speak in future of Draper's law.

Attempts to directly demonstrate the truth of this law in the case of such photo-sensitive compounds as the silver haloids are frustrated by the opacity of these salts, but there are other reasons for believing that the law applies in these cases. These reasons will I think be easily intelligible after our treatment of spectrum photography in the last lecture. If thin films of the silver haloids in suitable vehicles are examined by transmitted

light, it will be found that the absorption spectra are complementary to the photographic spectra. Let us understand the full significance of this fact. The maximum absorption, as shown by the spectral analysis of the transmitted light, coincides with the maximum of photo-decomposition as revealed by the developer after exposure to the spectrum. This means that the waves which are the most effective photographically are precisely those which are *absorbed* by the haloid—in other words Draper's law of the relationship between absorption and photochemical decomposition has a direct bearing upon photographic processes. This is not a merely inductive leap, but a conclusion which I must now attempt to justify in detail.

Perhaps the best proof of the existence of such a relationship between photographic sensitiveness and absorption is furnished by the optical change which is associated with the change in the state of molecular aggregation undergone by the silver haloids during the process of ripening. This subject has already been touched upon in a former lecture (p. 124) and we may now resume its con-

sideration with advantage. Commencing with silver bromide it will be remembered that in its unripened state it appears reddish by transmitted light, but as the particles grow by ripening less and less red is transmitted. What does this change imply? You will of course be prepared with the answer that the larger particles *absorb* more of the red. But if absorption means photochemical decomposition, as Draper's law leads us to expect, the ripened bromide should be more sensitive to red, and this is just what is found on photographing the spectrum. A large number of most carefully made experiments have been conducted by Dr. Eder and they all confirm this conclusion. Here are three of Eder's curves which will speak for themselves :—

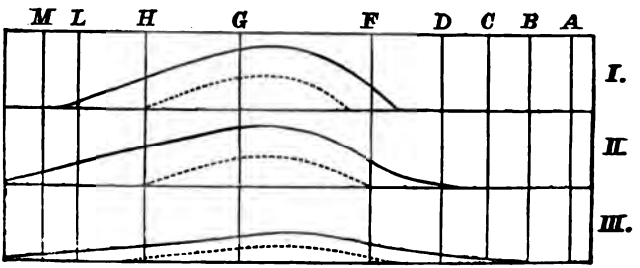


FIG. 10.—SPECTRA PHOTOGRAPHED ON DIFFERENT FORMS OF SILVER BROMIDE

No. I. represents the action upon the unripened bromide and No. II. the action upon the ripened haloid, both being emulsified in gelatine. The dotted curves show the effect of short exposure and the continuous curves the result of longer exposure. No. III. shows the effect of ripening almost up to the point of decomposition.

These curves are highly instructive taken in connection with the other purely chemical considerations which have been dealt with in former lectures. It will be seen that the position of the normal maximum for the bromide is not materially shifted—the effect of ripening is simply to extend the sensitiveness more towards the red. We see now why the ripened bromide is the more sensitive: it is affected by a wider range of spectral colours than when in the unripened condition. This is the optical justification of the statement which was made in the last lecture (p. 258) respecting the superiority of the bromide for rapid photography.

The general result of these and similar experiments is to show that the sensitiveness of the

silver haloids for particular rays is largely dependent upon their state of physical aggregation. This state is in its turn dependent upon the mode of formation of the haloid, the nature of the vehicle in which it is suspended, the state of dilution of the reacting solutions, &c. By appropriate treatment, the details of which I cannot now stop to explain, silver chloride is capable of being obtained in different states of molecular aggregation corresponding to the ripened and unripened forms of the bromide. As illustrating the influence of the vehicle, it has been found that the highly sensitive ripened form of the bromide is much more difficult to obtain in collodion than in gelatine. By taking certain special precautions however, Abney has succeeded in producing a form of the bromide in collodion which appears blue by transmitted light, and which is sensitive to rays far in the infra-red region of the spectrum.[1] This special form of emulsion is confessedly difficult to prepare; by its means it is possible to obtain photographs

[1] *Phil. Trans. Roy. Soc.* 1880, p. 653; *Ibid.* 1886, Part II. p. 457.

of the spectrum far beyond the lowest limit of visibility. The coarse-particled bromide is in this form susceptible even to waves of such low refrangibility as those emitted by a vessel of boiling water. The action of the spectrum upon this and the two modifications of the chloride is shown in the curves figured below:

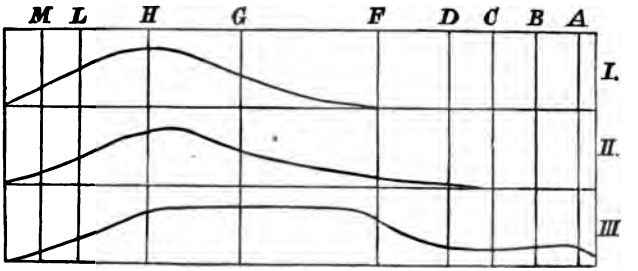


FIG. 11.—SPECTRA PHOTOGRAPHED ON DIFFERENT FORMS OF SILVER CHLORIDE (I. and II.) AND ON THE RED-SENSITIVE FORM OF SILVER BROMIDE (III.).

No. I. represents the ordinary form of the chloride in collodion, the film appearing red by transmitted light. No. II. is the same haloid emulsified in gelatine and *absorbing* more of the red; this form appears grey by transmitted light. No. III. is the photographed spectrum on the red-

sensitive form of the bromide in collodion prepared by Abney.

The results which have been laid before you in this lecture are of such importance that no excuse need be made for attempting to get a little further insight into the inner mechanism of the processes of absorption and decomposition which have been revealed. The general history of the progress of knowledge teaches us that the greatest advances are always made when one branch of science encroaches upon another. I might devote a whole course of lectures to the illustration of this principle. Consider for example the application of electricity to the decomposition of chemical compounds, resulting in the discovery of the compound nature of the alkalies and the isolation of the metals potassium and sodium; or take again the application of physical principles to the interpretation of the properties of gases leading to the law of Avogadro and the complete revolutionizing of the fundamental conceptions concerning the nature of chemical atoms and molecules. Coming nearer to our present subject, remember

the influence of the introduction of optical methods into chemical investigation resulting in the discovery of spectrum analysis with its far-reaching consequences. Looking at these curves showing the effects of a change in the state of aggregation upon the sensitiveness of the silver haloids, it is impossible to avoid coming to the conclusion that we may have in this phenomenon a point of contact between chemistry and physics which only awaits further development in order to lead to results of lasting importance to both branches of science.

That inherent property of a silver haloid molecule which causes it to undergo a maximum amount of decomposition per unit of time in a particular part of the spectrum is no doubt a result of the mechanical structure of the molecule. The rays are absorbed because the molecule or some constituent of the molecule has a period of vibration which is synchronous with the period of vibration of the ether-wave corresponding to that particular colour. We know absolutely nothing as yet of the internal mechanism of molecules, and I must caution you that I am

here entering upon speculative ground. It would be rash therefore to attempt to draw any close analogy between known physical phenomena which are capable of being explained mechanically, and that which occurs in a solid particle under the influence of light. The only comparison which it is safe to venture upon is that the absorption of light in these cases is analogous to the absorption of an air-wave corresponding to a definite note in music by a stretched string or a tuning-fork capable of emitting the same note when thrown into vibration. The string or tuning-fork can take up the sound in this case because its period of vibration corresponds with that of the air-wave [B].

But even this analogy does not take us very far, and if pressed too closely it may lead us astray altogether. It is sometimes asserted for instance that the absorbed impulses cause the molecule to swing as a whole, the amplitude becoming at length sufficient to cause one of the constituents to fly off. This may be the state of affairs, but it is also possible that the

absorbed impulses act upon one constituent of the molecule only. The former view would lead to the conclusion that in the case of the silver haloids the action of the blue rays is to cause photochemical dissociation. But we have learnt that this is not the case—we know that we must have a halogen absorbent present or the decomposition does not take place at all. The photo-decomposition may thus be in reality a mechanical function of the halogen atoms in contact with a second substance with which they can combine. This view appears all the more probable when we consider that both the silver haloids and all other photo-decomposable halogen compounds are most sensitive for the blue and violet rays, *i.e. the very colours which are most strongly absorbed by the halogens themselves* [C].

Any attempt to present a physical picture of what occurs in a silver haloid molecule during the process of ripening would take us still further into the region of speculation. We know for a fact that the particles grow in size during this process, so that the red-absorbing particle must

consist of a larger aggregate of molecules than the blue-absorbing particle. But how increase in size (and consequently in mass) affects the vibrating period of any one constituent of the system of molecules is at present beyond the reach of physical inquiry. An analogy might perhaps be useful here if employed with caution.

If we take a ray of light consisting of waves of some two or three vibrating periods only, such for instance as the light emitted by glowing hydrogen, and examine its spectrum, we see only certain bright lines in the positions corresponding to their respective refrangibilities. These bright spectral lines are the optical expressions of the mechanical structure of the hydrogen molecule—they indicate that the molecule is capable of vibrating in certain periods and thus of emitting waves of particular lengths. The width of the lines will of course depend upon the width of the slice of light which is passed through the prism, *i.e.* upon the width of the slit of the spectroscope. Now it has been shown by the researches of Plücker and Hittorf and of

Frankland and Lockyer and others, that, the diameter of the slit remaining unaltered, the width of these hydrogen lines goes on increasing as the pressure of the glowing gas is increased; in other words, the discontinuous spectrum tends to become continuous as the pressure increases. I cannot but think that there is a real analogy between this discovery and the spreading of the photographic spectrum of silver bromide as its particles become larger. A glance at the curves will show that the position of the normal maximum remains unaltered throughout. This maximum is the analogue of the position occupied by a bright line in the spectrum of a glowing gas, and the effect of an increase in the size of the haloid particle is analogous to the effect produced upon the spectrum of the gas by increase of pressure. In both cases the spectrum widens out in such a way as to make the discontinuous spectrum tend to become continuous: in other words, to the special vibrations corresponding to the maximum of luminosity in the emission spectrum or of absorption in the photographic spectrum, pressure

in the one case and increase of size in the other case, causes the addition of vibrations of both longer and shorter periods than those which may be regarded as the normal vibrations of the gas or of the haloid.

Such considerations as these lend countenance to the belief which has already been expressed, that it is not the molecule of the silver haloid as a whole which is responsible for the special photographic sensitiveness of the compound. The fact that the maximum remains while the particles go on growing seems to point most distinctly to the conclusion that the seat of photochemical action is intra-molecular. Were it otherwise we should expect to find such a distinct increase in size associated with a displacement of the maximum or with the appearance of a new maximum. The curves show that this is not the case—the maximum of decomposition still takes place about G, but to this major sensitiveness there is added a minor sensitiveness for the less refrangible rays, or, more correctly speaking, the feeble sensitive-

ness for the less refrangible rays is exalted to a practically workable pitch by the increase in size of the silver haloid particles. To bring this point home by a practical illustration I may add that, even with the red-sensitive form of the collodio-bromide emulsion, Abney has found that in order to impress the region about A an exposure twenty-five times greater than that required to photograph G is necessary, while the infra-red requires thirty-five times the exposure for G. The spectrum in this case was that of bright sunlight at noon.

The present position then, so far as concerns modern photographic processes, is that although the sensitiveness for such colours as yellow, orange, and red can be increased, we cannot with silver salts obtain a plate which is equally sensitive to rays of both high and low refrangibilities. Till this is done, or rather till a plate can be prepared which is sensitive to colours in the same order of intensity as we perceive them, no photographic picture will give an absolutely faithful representation of coloured objects—the

blues and violets will still give a stronger impression than the other colours. These more refrangible colours can of course be toned down by causing the light to pass through an absorbing medium, such as red glass, but although the less refrangible rays are given greater effect by this means, it is obvious that the total sensitiveness of the plate is lowered in consequence. The ideal state of perfection which is the aim of modern investigations, is to have a plate which shall without loss of sensitiveness record the actual visual intensities of the colours of an object in their correct values. Such a plate would be *orthochromatic.* It has already been pointed out that in all ordinary processes the silver haloid records its colour impressions in quite a different order to that in which they are recorded on the human retina: *the object of orthochromatic photography is to bring visual intensity and photographic intensity into harmony.*

The first step in this much-desired direction was made in 1873 by Professor H. W. Vogel, of Berlin, who discovered that the silver haloids could be made

sensitive to yellow and greenish-yellow by tinting the films (collodion) with certain coal-tar dyes such as corallin, aldehyde green, cosin, cyanin and many others. This discovery formed the starting-point of a series of investigations which have been carried on to the present time by various experimenters. I cannot stop to recount the different steps in the progress of this discovery, but must limit myself to a brief statement of the general results which have been arrived at. The main fact, that new maxima of chemical activity can be obtained in the less refrangible regions of the spectrum by the addition of dyes to the film, has been confirmed by the work of Becquerel, Waterhouse, Abney, Carey Lea, Eder and C. H. Bothamley. Now that gelatine emulsion is so generally used in photography, the practical aspect assumed by the problem is the rendering of such films orthochromatic by the addition of suitable colouring matters. Immense numbers of dyes have been tried under various conditions, especially by Dr. Eder of Vienna. The only point of manipulation which it is necessary to explain is that the film may be dyed by adding a solution of the colour-

ing matter to the emulsion itself, or the coated dry plate may be dipped in the coloured solution and when dyed withdrawn and dried. The amount of colouring matter employed is also a point of importance, since too little or too much both act detrimentally with respect to special sensitizing action. According to some recent experiments of Abney's it is not even necessary to dye the film, but the same effects are produced by coating the sensitive surface with a varnish containing the colouring matter.

The importance of this new departure will be sufficiently obvious from the general considerations which have been submitted in the course of the present lecture. The first thing that must be realized before we can proceed to discuss the chemical bearing of the discovery, is the precise way in which these dyes influence the photographic spectrum. The following series of curves selected from the results of Eder and Abney[1] will show how the

[1] Eder's curves (I. to X.) are taken from a paper by C. H. Bothamley in the *Journ. Soc. Chem. Ind.* for 1887, p. 425. Abney's curves (XI. to XIV.) are selected from a series given in the Conference number of the *Journal of the Camera Club*, March 16th, 1888, vol. ii. p. 58.

colouring matters affect the less refrangible end of the spectrum.

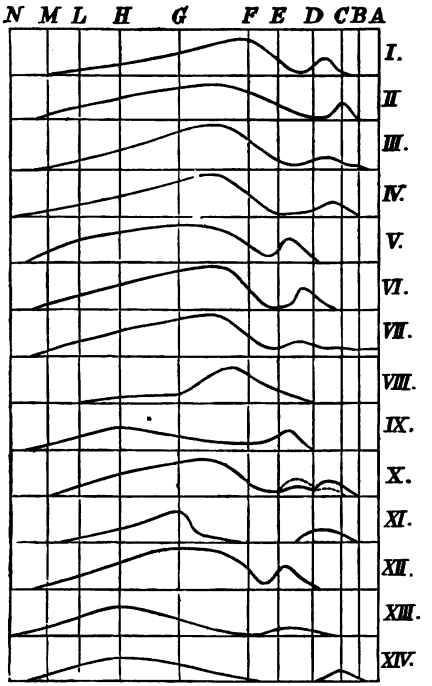


FIG. 12.

I. Violets; II. Greens; III. Iodine green; IV. Cyanin; V. Eosin; VI. Ammoniacal rose Bengal; VII. Cœrulein; VIII. Chrysaniline; IX. Eosin on AgCl; X. Eosin + Cyanin; XI. Erythrosin on AgI + $AgNO_3$; XII. Erythrosin on AgBr; XIII. Erythrosin on AgCl; XIV. Cyanin on AgCl. Where the haloid is not specified AgBr has been used.

With respect to these curves it must be borne in mind that they show nothing more than the relative

sensitiveness of the dyed film for the different regions of the spectrum. They tell us nothing of the absolute sensitiveness of the plate. The new maximum in the less refrangible region is often acquired at the expense of a general diminution of sensitiveness at the more refrangible end, so that a longer exposure has to be given to bring out the special sensitizing action of the dye: in other words the total sensitiveness of the plate is lowered. Then again it must be observed that for the colouring matters used and under the particular conditions of the experiments, the maximum of action is still in the more refrangible region. This means that such dyed plates, although relatively more sensitive to green, yellow, orange, or red than they were before, are still possessed of greater sensitiveness for violet and blue, so that in photographing a coloured object on one of these plates it would still be necessary to tone down the blue and violet by interposing an absorbing medium, such as yellow glass. Even with the best of orthochromatic plates it seems that some such yellow screen is necessary before a coloured object can be

photographed with all the colours represented in their true gradations of brightness. Another point which an inspection of these curves brings out is that the same dye produces different effects with the different silver haloids. This will be seen on comparing V. and IX. showing the action of eosin on the bromide and chloride respectively, and XI. XII. and XIII. showing the action of erythrosin on the iodide, bromide, and chloride.

In its practical applications orthochromatic photography is most likely to be serviceable where distinct differences of colour have to be reproduced, such as in the copying of paintings. It will be readily understood also that an orthochromatic plate would be valuable in cases where we have to employ artificial light, like gas or candle light, which is relatively poor in the more refrangible rays, because in such a plate the sensitiveness for the less refrangible rays is exalted by the action of the dye. In continuing the experiments in this direction, Mr. C. H. Bothamley, of the Yorkshire College, Leeds, has succeeded in preparing plates which are more sensitive to yellow and orange than

to blue and violet, and which thus approach the ideal coincidence between visual and photographic intensity. The result of this recent work is, that of the numerous colouring matters tested, ammoniacal erythrosin appears to be the most effective sensitizer for the yellow, and ammoniacal cyanin for the orange.[1] It will be instructive to inspect the accompanying curves taken from Mr. Bothamley's paper and showing the effects of some of the most active sensitizers upon gelatino-bromide emulsion:—

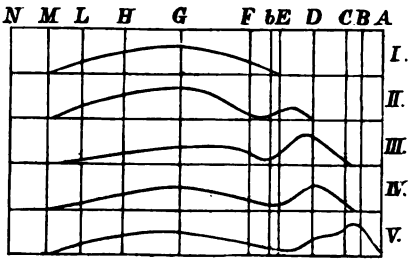


FIG. 13.

I. Gelatino-bromide (undyed); II. Ammoniacal Eosin; III. Ammoniacal Erythrosin; IV. Ammoniacal Rose Bengal; V. Ammoniacal Cyanin.

[1] A number of photographs taken by Mr. Bothamley were projected on the screen. These showed in a very striking manner the difference between the pictures of coloured objects, such as flowers, coloured papers, &c., taken on ordinary plates, and on plates dyed with ammoniacal erythrosin, both with and without the intervention of a yellow glass screen.

It is generally admitted by practical photographers that the seeds sown by Vogel in 1873 are likely to develop into results of the highest value to the art. But although the utility of orthochromatic photography has been proved in many ways, it must be confessed that, so far as the scientific aspect of the discovery is concerned, we are at present only on the threshold of an unknown region. There are many discrepancies in the very facts themselves, and different workers are by no means concordant in their results. From a chemical point of view the data require purification —not only figuratively, but also literally. There is no doubt that most of the discrepancies have arisen from the use of commercial specimens of the colouring matters instead of the pure chemical compounds, and the action of the dyes has thus been complicated in unknown ways. For this reason the results are hardly ripe for discussion as yet, and I cannot do much more than lay before you the existing views respecting the principles at work.

If we sum up the evidence at present available, the one general outcome which appears to be of

the most significance is, that there is a distinct connection between the specific absorption of the dye and its sensitizing action. In order to find out in which part of the spectrum the sensitizing action will be exerted, it is only necessary to examine the absorption-spectrum of the dyed film itself—where the dark absorption-band of the colouring matter appears, there will be a new maximum on exposure to the spectrum and development [D]. It must however be borne in mind that this holds good only for colouring matters which act as special sensitizers. It by no means follows because a colouring matter shows a definite absorption-spectrum, that it will necessarily sensitize for the region where absorption takes place: in other words, absorption may or may not be associated with special sensitizing action. Indigo for instance absorbs the yellow, but does not sensitize a film for this colour. Then there is another point which must not be overlooked in stating the connection between absorption and sensitizing action, and that is that the coincidence between the absorption-band and the region

sensitized is only true when we examine the absorption of the dyed film itself, *i.e.* of the coloured gelatino-bromide emulsion when dry. The coincidence is said by Vogel and Eder not to hold good when the spectrum developed on a dyed gelatino-bromide film is compared with the true absorption-spectrum of the dye in aqueous or alcoholic solution, or in a plain gelatine film containing no silver haloid. The association of the dye with the silver haloid is said by these observers to cause a slight shifting of the absorption-band, towards the red, so that the second maximum in the developed image is a little on the less refrangible side of the absorption-band shown by the spectrum of the colouring matter in vehicles containing no silver haloid.[1] But here again I must caution you against receiving these statements as final, because other workers have failed to obtain this shifting of the maximum.

[1] This displacement of the band of absorption (and chemical activity) towards the red is believed to be in accordance with Kundt's law, which asserts that the absorption-band of a colouring matter is displaced towards the red as the refractive power of the medium in which the substance is dissolved increases.

No theory of the action of sensitizing colouring matters upon the silver haloids can be as yet regarded as conclusively established. There seems to be no connection between the chemical constitution of the colouring matters and their sensitizing action; neither is there any connection between their fluorescent properties or their power of anomalous dispersion and their action as special sensitizers. Two distinct classes of hypotheses are current, one physical and the other chemical. According to the older view the vibrations absorbed by the dye are transferred to the silver salt and thus render the latter sensitive in the region of absorption. Some such idea as this appears to have influenced the course of experimental work in the early days of the discovery, and the colouring matters were in accordance with this view spoken of as "optical sensitizers." This physical theory has however been modified, chiefly through the researches of Eder, who has shown most conclusively that the silver haloid is actually dyed by the colouring matter, the silver salt forming a compound of the nature of a lake with the dyestuff.

Whether these compounds of the silver haloid with the colouring matter are truly chemical, or whether they are "molecular," *i.e.* physical, need not concern us now, but Eder's experiments clearly prove their existence. Starting from this fact, the authority just named supposes that the vibrations are absorbed by the coloured compound, whatever the latter may be, the energy of the absorbed vibrations being chiefly spent in doing the work of photochemical decomposition. The same vibrations absorbed by the dye alone, in the absence of the silver haloid, are chiefly converted into heat and do but little chemical work.

Against these physical hypotheses there is much to be urged on *a priori* grounds, but it will be safer to confine ourselves to the results of experiment. According to Abney the action is purely chemical, the colouring matter undergoing photochemical decomposition (by oxidation or otherwise) in the region of absorption and giving rise to products which act as reducing agents upon the silver haloid. The fact that the best sensitizing colouring matters are just those which are known to be most easily

affected by light, such as the phthaleïns (eosin group) and cyanin, is strongly in favour of the chemical hypothesis. Let me remind you of the bleaching action of light upon a sheet of paper dyed with eosin, shown in the first lecture (Exp.N, p. 34).

Now the chief difficulty which chemists will experience in accepting this explanation is, that the dyestuff should by photochemical decomposition give rise to products which exert a reducing action upon the silver haloid. But this difficulty arises from our ignorance of the nature of the products formed under these conditions. It must be remembered that the molecules of these colouring matters are extremely complex, as will be seen from the following empirical formulæ of a few of the most active :—

Eosin	$C_{20}H_6Br_4O_5K_2$
Rose Bengal	$C_{20}H_2Cl_4I_4O_5K_2$
Erythrosin	$C_{20}H_6I_4O_5K_2$
Cyanin (quinoline blue) . .	$C_{29}H_{35}N_2I$.

It is not to be wondered at that among the products of decomposition of compounds having such highly complicated molecules as these dyes, there

should be substances of a reducing character. Thus an active reducing agent, formic acid, has already been stated (page 22) to be among the products of the oxidation of gelatine by potassium dichromate under the influence of light, so that the production of a reducing agent by the photo-oxidation of a highly complex molecule is not without a parallel.

There are other considerations which tell in favour of the chemical hypothesis, such for instance as the fact that the addition of ammonia increases the special sensitizing action of the dyes, but some of the experiments described by Abney appear to me to prove most conclusively that it is in this direction that we must look for the explanation of the phenomenon. The nature of the evidence furnished by these experiments will be best appreciated from a brief description of a few typical cases :—

A plain collodion film dyed with eosin was exposed to the action of the spectrum ; a bleached band appeared in the green in the position of the absorption-band seen in the spectrum of the light transmitted through the film. The plate was then coated

with a collodio-bromide emulsion, allowed to dry, and then developed. A dark band appeared in the position occupied by the bleached band before the application of the emulsion and development. On repeating the experiment with cyanin the same result was obtained, only the bleached band was in the orange and the dark band, after development, in the same position. Then again other experiments were conducted with collodio-chloride films tinted with cyanin and exposed to the spectrum till the latter was visibly printed. Now on the physical hypothesis we should expect to find two maxima of photo-reduction under these circumstances, one in the violet and the other in the region of absorption, *i.e.* in the orange. But there was nothing of the kind—the normal maximum of decomposition showed itself in the violet, but the orange band was *bleached* as before. With short exposure both the violet and orange maxima came out dark on development, showing that the decomposition of the dye in the orange had given rise to products which reduced the silver haloid sufficiently to enable it to give a dark band on development. Similar experiments

were made with gelatino-chloride films with the same result, and, what is still more striking, it was found that the dye exerted its action if the plate was coated with a plain collodion or varnish film coloured with cyanin, and then exposed to the spectrum and developed. Even when the dyed collodion or varnish was washed away from the gelatino-chloride film after exposure, the orange maximum could be developed, showing that the reducing product of the decomposition of the dye had done its work. Many other experiments were made with the other haloids both with cyanin and erythrosin, and all leading to the same conclusion, viz. that it is the action of the spectrum on the colouring matter in the region of absorption, and not upon the silver haloid itself, which gives rise to the second maximum in the spectrum photographed on an orthochromatic plate. I regret much that time will not permit me to give a more extended account of these interesting experiments,[1] but I have

[1] The original description of the experiments will be found in the Conference number of the *Journal of the Camera Club*, March 16th, 1888.

described a sufficient number to enable you to see that their general drift is to disprove the physical hypothesis and to substitute chemical action.

Before taking leave of this part of the subject I am tempted to offer a suggestion which may be of use in guiding future experiments. The chemical hypothesis of orthochromatic action rests upon the fact that the best special sensitizers are the most fugitive dyes. Now there is reason for believing that the bleaching of a colouring matter by the action of light is due to photochemical oxidation. If this be the case atmospheric oxygen may be essential for the production of orthochromatic effect, and the formation of a second maximum in the less refrangible part of the spectrum might be prevented by immersing the dyed plate in a reducing solution, or in some inert liquid or gas which prevented access of air. Experiments of this kind might easily be made, and if the action in the green, yellow, or orange, did not take place under these circumstances, the chemical hypothesis of orthochromatic photography would be raised to the rank of a proved theory, while on the other

hand, if the second maximum still appeared, this hypothesis would not be disproved, because it is possible that the breaking down of the complex molecule of the colouring matter by the action of light might take place in the absence of oxygen, and thus also give rise to the formation of products of a reducing character.

Before we have finished with the action of the spectrum on the silver haloids, I have to call attention to a special property of the chloride which has long been known, and which is of interest in connection with the greatest of all photographic problems—the direct and permanent reproduction of the camera picture in its natural colours. Let me state at once, in spite of occasional rumours or sensational newspaper paragraphs, that this problem has never been solved. The only approximative attempts have been rendered possible by the fact that silver chloride is capable, under certain conditions, of receiving an impression of the spectrum in which the colours more or less approach the natural spectral colours.

The first observations in the direction indicated were made by Seebeck in 1810, and the subject was more closely investigated thirty years later by Sir John Herschel. The experiments went to show that when a surface of silver chloride on paper was exposed to white light till it became violet, the spectrum then impressed itself on the chloride, after a lengthened exposure, in colours approximating to the natural hues. Other investigators have carried on the work under different conditions, and have confirmed the general result that silver chloride can be made susceptible of photochromatic impressions. In 1847–48 and 1855, E. Becquerel made known his experiments with polished silver plates, which were covered with a film of violet chloride by a brief immersion in cupric chloride or other chlorinating solution, and then exposed to the spectrum; such films recorded the colours in the same way as Herschel's violet chloride paper. Similar results were obtained by Niepce de St. Victor (1851–66), by Poitevin (1865), by Zencker (1868), and quite recently by Carey Lea upon the red

photochloride which has been alluded to in a former lecture. A modification of the method which has lately been described by G. Staats,[1] enables me to show you an approximation to photochromatic printing which will serve to illustrate the general nature of the results. A copper plate has been silvered by electro-deposition, and the polished surface covered with a slate-coloured film by a brief immersion in a solution of ferric chloride. Various coloured glasses have been placed in contact with the film and the whole exposed to sunshine. On removing the coloured glasses it is seen that under each glass there is a colour approximating somewhat to that of the glass—the correspondence is not very perfect, but is sufficiently distinct to enable you to see that each glass has given a differently coloured impression [E].

These experiments have not yet led to any practical issue, because the colours cannot be fixed, but from a chemical point of view the line of work opened up by them promises to be of interest.

[1] *Ber. Deutsch. Chem. Gesell.* 1887, p. 2322.

The photochromatic property apparently belongs to the reduction product, which we now have good reasons for believing to be an oxychloride. It may at first sight appear improbable that the coincidence between the colours of the spectrum and the colours of the impressed film is a mere accident; but although this is difficult to believe I venture to think that it is an accidental coincidence and nothing more. By this I mean to say that there is no connection of a physical nature between the vibration-period of the ether-waves and the colours assumed by the reduction product—the connection probably arises from the production of different compounds in different parts of the spectrum, and it happens that the colours of these compounds approach somewhat in shade to those of the corresponding spectral colours. In the best specimens of these photochromatic spectra that I have ever seen, the colours were certainly nothing more than approximations to the pure spectrum colours, and even in these spectra some of the coloured effect was due to the unaltered ground colour of the film, in

regions where some particular colour had produced no action at all.

Of the chemical nature of these differently coloured products we know absolutely nothing. According to Carey Lea the purple forms of the photochloride do not give such good results as the red forms. Violet, blue, and red glasses produce distinct photochromatic impressions upon the red photochloride; green produces but little effect, and yellow is capricious in its action. G. Staats has recently made some experiments,[1] having for their object the isolation of the different coloured products, but after dissolving the colours off the silvered plate by ammonia, no other product than Carey Lea's red photosalt could by any means be obtained. The coloured products are destroyed by the action of the solvent, and all the colours when heated on the plate are, according to Staats, converted into the red photochloride. By allowing thin silver foil to float in ferric chloride solution for a few seconds till distinct colours were produced, this same experimenter

[1] *Ber. Deutsch. Chem. Gesell.* 1888, p. 2199.

succeeded in obtaining films of a violet and red colour from which the excess of silver could be dissolved out by nitric acid, the films thus treated retaining their original colours. Until we have analyses of these coloured products it is useless to attempt to speculate as to their chemical nature, but a survey of all the facts available makes it not improbable that we may have in these cases oxychlorides or compounds of oxychlorides with unaltered chloride containing varying proportions of water of hydration or constitution. Beyond this it would be at present unsafe to venture in attempting to deal with the chemical principles of photochromy.

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[1] *Ber. Deutsch. Chem. Gesell.* 1888, p. 2109.

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uniformity in nomenclature if photographers would generally adopt this necessary alteration. The double salt formed by the action of the thiosulphate upon the silver haloid is a silver sodium thiosulphate :—

$$2AgBr + 3Na_2S_2O_3 = Ag_2Na_4(S_2O_3)_3 + 2NaBr.$$

The solid crystalline double salt has the formula $Ag_2Na_4(S_2O_3)_3,2H_2O$.

It is well known that a strong solution of thiosulphate is necessary in fixing; if the solution is too weak, instead of the extremely soluble double salt there is formed another insoluble double salt of the formula $AgNa(S_2O_3),H_2O$, which would remain in the film [A]. It is only necessary to point out in dismissing the chemical action of fixing agents that the potassium cyanide of commerce is always alkaline and has a tendency to soften the gelatine film. This salt moreover has a slightly solvent action upon metallic silver, and thus tends to reduce the intensity of the image in the medium tones: for these reasons sodium thiosulphate is safer as a fixing agent.

It sometimes happens that a negative after development and fixing is found not to have sufficient density for printing purposes. This defect, which may arise from insufficient exposure or under development or other causes, is remedied, as all photographers know, by a process of intensification. There are many intensifiers in use, and I shall have to limit my remarks to a few of the best known substances employed for this purpose. In the old collodion process the image was often intensified by the application of a further quantity of an acid ferrous sulphate or pyrogallol developer to which a little silver nitrate had been added just before use. The silver image was thus enabled to go on increasing in density by the same process as that by which it was originally formed. It is evident that this operation is nothing more than a continued development.

In the case of gelatine films the use of a silver intensifier is objectionable because of the tendency of gelatine to retain soluble silver salts. Of the various intensifiers now in use, mercuric chloride followed by the application of

other substances is recommended by many practical photographers, and it will be instructive to follow out the chemistry of this process. If a negative is immersed in a solution of mercuric chloride the dark image becomes bleached, owing to the reduction of the mercuric salt to mercurous chloride by the metallic silver, as was pointed out by Herschel in 1840 [B]:—

$$Ag_2 + 2HgCl_2 = 2AgCl + Hg_2Cl_2.$$

The image is thus transformed into a mixture of silver chloride and mercurous chloride, both being white and insoluble, but not sufficiently opaque to enable the negative to be used for printing. After washing off the bleaching solution, the white picture is therefore darkened by being washed over with some other solution which effects the necessary change in colour. Thus, by using a dilute solution of ammonia the silver chloride is dissolved out and the mercurous chloride transformed into the dark dimercurous-ammonium chloride [C]:—

$$Hg_2Cl_2 + 2NH_3 = NH_2Hg_2Cl + NH_4Cl.$$

Sometimes ammonium sulphide is used, in which case the mixture of silver and mercurous chlorides is transformed into a mixture of the sulphides. Or again, the bleached picture may be darkened by the application of sodium sulphite [D], which reduces the mercurous chloride to mercury, or by potassio-ferrous oxalate, which reduces both the silver and mercurous haloids to the metallic state [E]:—

$$Hg_2Cl_2 + Na_2SO_3 + H_2O = 2Hg + Na_2SO_4 + 2HCl$$

$$2AgCl + 2FeC_2O_4 + K_2C_2O_4 = Ag_2 + Fe_2(C_2O_4)_3 + 2KCl$$

$$Hg_2Cl_2 + 2FeC_2O_4 + K_2C_2O_4 = 2Hg + Fe_2(C_2O_4)_3 + 2KCl$$

Such an intensifier as potassio-ferrous oxalate thus restores the image in silver and mercury, the total density being obviously much increased. By again treating such an image with mercuric chloride and repeating the application of ferrous oxalate, a further increase in density is given, and so the process can be repeated any number of

times in succession till the necessary opacity is obtained. Another intensifier recommended by many workers for gelatine plates is a solution of potassio-silver cyanide, prepared by adding potassium cyanide to silver nitrate till the precipitate first formed is nearly all redissolved. This solution is applied to the image bleached by mercuric chloride [F].

The action of potassio-silver cyanide upon mercurous chloride gives rise to the formation of a dark product which contains a large amount of silver, but the substance is a complex mixture containing also mercury, cyanogen, and a trace of chlorine.[1] Silver appears to be the chief constituent and its formation may take place according to the reaction :—

$$Hg_2Cl_2 + 2AgK(CN)_2 = Ag_2 + 2Hg(CN)_2 + 2KCl.$$

[1] This statement is based on a series of analyses of the dark product, obtained by allowing a solution of potassio-silver cyanide to remain in contact with freshly precipitated and washed specimens of mercurous chloride for periods varying from seventeen hours to fourteen days. The experiments were made at the Finsbury Technical College by two students of the Chemical Department, Messrs. J. M. Smith and J. H. Coste.

Another class of intensifiers is typified by such compounds as the ferricyanides of uranium and lead, the first of these having been introduced by Selle, and the second by Eder and Tóth. If the silver image is washed with a solution of a ferricyanide, the latter becomes reduced to ferrocyanide. Thus in the case of lead ferricyanide :—

$$2Ag_2 + 2Pb_3Fe_2(CN)_{12} = Ag_4Fe(CN)_6 + 3Pb_2Fe(CN)_6$$

The silver image thus becomes converted into a denser picture composed of a mixture or possibly of a compound of the ferrocyanides of lead and silver. Both these salts are white, and in order to darken them and render them opaque, the plate, after the intensifying solution has been thoroughly washed out, is treated with a solution of ammonium sulphide so as to convert the ferrocyanides into the dark sulphides of the metals. The action of Selle's uranium intensifier is similar in principle, only the uranic ferrocyanide, being of a dark brown colour, at once intensifies the picture without the subequent application of a darkening agent such as mmonium sulphide. The metallic ferricyanides

used in these intensifiers are prepared by double decomposition between a soluble salt of the heavy metal and potassium ferricyanide ; *e.g.* :—

$$3Pb(NO_3)_2 + K_6Fe_2(CN)_{12} = Pb_3Fe_2(CN)_{12} + 6KNO_3.$$

The intensifiers most generally used having thus served to illustrate the general chemical principles involved in the process, it is unnecessary to dwell much longer upon this part of the subject. I may just point out that of the numerous intensifiers proposed by various operators, some act in the simplest possible way by substituting another metal for the silver of the image. This is the case, for instance, with auric and platinic chlorides :—

$$3Ag_2 + 2AuCl_3 = Au_2 + 6AgCl$$
$$2Ag_2 + PtCl_4 = Pt + 4AgCl.$$

The selection and practical application of the intensifier most suitable to any particular kind of negative is a matter of individual judgment and experience, but if I attempted to deal with

this I should be going beyond my present limits, which, as you are fully aware, do not comprise photographic manipulation.

The weakening of a negative which by over exposure or over development has given too dense an image, is another problem which the photographer sometimes has to deal with. In this case the silver deposit has to be thinned down by the use of an appropriate solvent. The chemical conditions which have to be met are simple enough, although the practical application of the method is, as in the case of intensification, a matter of skill and judgment. The substances generally employed are those which are capable of partially converting the metallic silver into a salt which can be immediately dissolved away. Two of the weakening solutions in use will serve to illustrate the principle of action. I shall speak of these substances as "weakening agents" in order to avoid the use of the term "reducing agents," which has a totally different chemical meaning.

It is well known that a silver plate can be coated with a film of chloride by immersion in a solution

of ferric or cupric chloride: in other words silver *reduces* these salts [G]:—

$$Ag_2 + 2CuCl_2 = 2AgCl + Cu_2Cl_2$$
$$Ag_2 + Fe_2Cl_6 = 2AgCl + Fe_2Cl_4.$$

It would thus appear sufficient to wash the image with one of these chlorinating solutions so as to cover the silver superficially with chloride, and then dissolve off the chloride with sodium thiosulphate. Such a method of weakening would no doubt be effective, but it would be attended by a serious practical difficulty, and that is that the operator would not be able to ascertain to what extent the chlorinating solution had acted till after the removal of the silver chloride, and then he might find too late that the action had gone too far. The weakening agents now in vogue have therefore been devised with the object of enabling the operator to see the course of the action of the solution, so as to stop the process at the desired stage. The two weakening agents which I have selected as types have been introduced by Eder and Farmer respectively, and they both depend upon the reducing action of the silver of the image

upon a ferric salt, and the simultaneous removal of the silver salt thus formed by sodium thiosulphate. Thus in Eder's process a solution of potassio-ferric oxalate is prepared by adding ferric chloride to potassium oxalate, and this solution, immediately before use, is mixed with a solution of sodium thiosulphate. On washing the plate with this mixture the silver in the first place forms an oxalate, which is immediately removed by the thiosulphate :—

$$Ag_2 + Fe_2(C_2O_4)_3 = Ag_2C_2O_4 + 2FeC_2O_4$$
$$Ag_2C_2O_4 + 2Na_2S_2O_3 = 2AgNaS_2O_3 + Na_2C_2O_4.$$

Farmer's solution, which is generally used as a weakening agent for gelatine plates, is a mixture of potassium ferricyanide and sodium thiosulphate. The silver in this case first becomes converted superficially into ferrocyanide, and the latter is then dissolved by the thiosulphate :—

$$2Ag_2 + 2K_6Fe_2(CN)_{12} = Ag_4Fe(CN)_6 + K_4Fe(CN)_6$$

$$Ag_4Fe(CN)_6 + 4Na_2S_2O_3 = 4AgNaS_2O_3 + Na_4Fe(CN)_6.$$

When a finished negative has been produced, the next operation is to obtain a positive print from it. Of the printing processes now in use, the ordinary albumenized paper process is the most generally employed, and is therefore no doubt the most familiar to you, so that we may commence with this method. In order to prepare the paper for printing it is first coated with a solution of salted albumen, the latter substance being obtained from the whites of eggs, and the salt used being ammonium chloride. When dry the albumenized paper is sensitized by being floated for a short time on a silver nitrate bath, after which it is allowed to drain and dry. Now the first point that concerns us is the chemical nature of the sensitive surface prepared in this way. The ammonium chloride of course forms silver chloride by double decomposition, but the sensitiveness of the surface is not due to silver chloride only, because the albumen also forms a compound with the silver of the nitrate—a fact which has already been alluded to (p. 117). The nature of the compound which is formed when a soluble silver

salt is added to a solution of albumen is quite unknown, but this need not surprise us when we bear in mind the fact that we know practically nothing of the chemical nature of albumen itself. The empirical formula generally assigned is (after Lieberkühn) $C_{72}H_{112}SN_{18}O_{22}$; but there is really at present no satisfactory evidence that the substances found in the animal and vegetable kingdom, and grouped by chemists under the general name of "albumenoids," are definite chemical compounds at all. Those who are acquainted with the methods of organic analysis will see that the formula of a compound having any approach to the complexity indicated above, cannot be deduced from analytical results with any degree of reliability.

Whatever may be the true constitution of albumen, it is at present only essential that you should recognize its property of forming an insoluble compound with silver nitrate [H]. Whether this substance is a salt or a molecular compound matters little, but, like all other organic silver compounds, such as the "gelatino-nitrate" referred to

in a former lecture (p. 118),[1] it is decomposed by light with the formation of a reddish-brown reduction product, and this is the property which is utilized in the printing process which we are now considering. The sensitive surface in this process consists therefore of a mixture of silver chloride and silver "albumenate," together with the excess of silver nitrate. The negative is placed in close contact with a sheet of this prepared paper, and is, as you all know, exposed to light till the positive image is visibly printed to a somewhat deeper shade than is actually required in the finished print. With respect to the chemical composition of the positive print at this stage all that can be said is that it is formed of a mixture of the photo-reduction products of silver chloride and silver "albumenate." The silver nitrate no doubt acts as a sensitizer towards the chloride, but it is improbable that it plays this part towards the organic silver compound.

[1] Certain organic bases belonging to the group of "anhydro-bases" give gelatinous precipitates with ammoniacal silver nitrate which darken on exposure to light, and in their general appearance and properties are very suggestive of the silver compounds formed by albumen and gelatine. See a paper by the author and F. W. Streatfeild, *Journ. Chem. Soc. Trans.* 1887, p. 699.

Instead of using a printing surface in which the silver chloride and organic silver compound are formed together, as in the process just described, the silver haloid may be emulsified in some organic vehicle and the paper or other printing surface coated with the emulsion. Several of these emulsion printing processes are in use. Thus a collodio-chloride emulsion was introduced by Wharton Simpson in which silver chloride is emulsified in collodion, and citric acid added to play the part of an organic sensitizer. A gelatino-chloride emulsion has been introduced by Abney in which a mixture of silver chloride and citrate is emulsified in gelatine in the usual manner, and then washed as previously described (p. 123) to remove the excess of soluble salts. For the various modifications and the modes of application of these printing emulsions I must refer you to the practical treatises. From a chemical standpoint it is important to remember that the action of light upon these emulsions is allowed to continue up to the stage of visible decomposition, and is not stopped at the formation of an invisible image. The printed picture in

all these cases is therefore composed of a complex mixture of the reduction products of the silver haloid and of the organic silver compound.

There is another method of obtaining silver prints which is now very frequently employed, and which combines both printing and development on the same surface. In this process, advantage is taken of the extreme sensitiveness of gelatino-bromide emulsion, paper coated with this emulsion having been recently introduced by the Eastman Company. It would be superfluous for me to say anything further about the chemistry of this method, as the principles have been amply dealt with in former lectures. This bromide paper can be used for contact-printing from a negative in the usual way, only, instead of exposing up to the stage of visible decomposition, a short exposure is given, and the invisible image developed by ferrous oxalate; the print is then washed and fixed as in the ordinary gelatino-bromide dry plate process. The positive picture is therefore in this case composed of metallic silver, and has in consequence a very different "tone" to the ordinary albumenized silver prints. One

advantage possessed by this bromide paper is that the great sensitiveness of the emulsion for rays of low refrangibility enables a print to be made by means of artificial light, such as lamp light or gas light, and the same property of the film enables it to be used for the production of enlarged prints. It is only necessary to put the negative into a kind of magic-lantern, and throw its image, magnified by the lens up to the desired scale, on to a sheet of the bromide paper and expose, develop, and fix as usual. With an ordinary paraffin lamp with a metallic reflector behind it in the lantern, an exposure of three minutes has been found sufficient to give an enlarged image from a quarter-plate negative on a sheet of paper 12 × 10 inches in area. Some of the results obtained by this method of enlargement have been forwarded by the Eastman Company for inspection. In looking upon these pictures it is interesting to reflect upon the accumulated experience which has rendered it possible for the modern photographer to take a negative in a very few seconds, and to obtain from it an enlarged positive print, using only such

sources of light as would have been quite inadequate to produce any impression on the sensitive films employed before the introduction of gelatine emulsion.

Returning to the question of the chemical composition of the image printed on a surface composed of silver chloride and some organic compound of silver, such as the albumenate, the most obscure point is the nature of the reduction product of the organic silver compound. There is a wide field for investigation in this direction, because it would appear from certain experiments which have been made from time to time, that we may have reduction products of organic silver compounds which are analogous to the oxyhaloids or photosalts. This is a very interesting point in connection with the chemistry of silver compounds, and it is all the more important because we know absolutely nothing of the nature of these organic silver reduction products. The evidence which justifies the belief that these products are the organic analogues of the haloid photosalts may be very briefly summarized.

In the first place an albumenized glass plate coated with silver albumenate by immersion in a silver nitrate bath gives an image on exposure which can be developed by means of pyrogallol. This observation was made by Monckhoven in 1863, and its importance in connection with the present subject consists in the fact that no silver haloid is present in the film, so that the image is formed entirely by the photo-decomposition of the albumenate. In the next place we get more distinct evidence in the same direction from certain experiments on what is called "image transference" which have been recently made by Carey Lea. In order to give a clear notion of what is meant by "image transference," I will first describe an experiment which was made by Eder and Pizzighelli in 1881. An invisible image was formed on a plate coated with silver chloride, and then, before development, the plate was treated with a solution of potassium bromide. Now it is well known that silver chloride is decomposed by this last salt :—

$$AgCl + KBr = AgBr + KCl.$$

The unaltered silver chloride is thus converted into bromide, and not only this, but the reduction product (photochloride) is also transformed into the analogous photobromide—the image becomes transferred from the chloride to the bromide, and the reduction product of the latter can be developed as usual after the plate has been washed. The experiment is not striking enough as a lecture demonstration to warrant its repetition before you, but chemically it is of great importance. Supposing the reduction products to be oxyhaloids the change may be thus represented :—

$$Ag_4OCl_2 + 2KBr = Ag_4OBr_2 + 2KCl.$$

Now Carey Lea has accomplished for the organic silver compounds what Eder and Pizzighelli have done for the chloride. He has found that such salts as the tartrate, citrate, oxalate, benzoate, &c., are capable of receiving an invisible image which can be transformed into the corresponding haloid reduction product by treatment with hydrochloric or hydrobromic acid, and the image thus transferred can be developed as usual. The full

significance of this observation will appear if I repeat one of the experiments [I]. A sheet of paper coated with silver tartrate is exposed for about a minute to the electric light. In accordance with the general notions of photo-decomposition we may now expect to have a surface formed of the reduction product of the tartrate. On removing the paper and painting a design upon it with dilute hydrochloric acid, we have a design in photochloride on a background of what I may provisionally call phototartrate. The latter compound is capable of development, but it does not give such a dense image as the photochloride, so that on tearing the paper in half and developing one portion with ferrous oxalate the design comes out black on a dark ground. From the other half of the paper the phototartrate can be completely removed by immersion in dilute nitric acid, which does not attack the photochloride. Now, on washing and developing this other half, the design comes out black on a white ground. Such experiments as this point to the formation of organic silver reduction products, and it is possible that

the darkened "gelatino-nitrate" or albumenate of silver may consist of such compounds. It is for this reason that I have directed attention to the subject of image transference in connection with the theory of silver printing.

Whatever may be the actual chemical composition of the image printed on a surface of albumenized paper sensitized in the manner already described, the reddish-brown colour of this image is objectionable, and it is accordingly modified by a subsequent operation known as "toning." This last process consists in depositing on the darkened portions of the print a finely precipitated powder of reduced gold or some other metal, which changes the reddish colour of the mixed reduction products into the tone so familiar in finished silver prints. In practice, gold-toning is now most generally in use, the print being first washed and then immersed in the toning-bath till the desired shade is reached.

The toning-bath contains a neutral solution of auric chloride, $AuCl_2$, as its active constituent,

the salt being generally supplied in the form of the double salt, $NaAuCl_4 2H_2O$, which is obtained by evaporating a solution of common salt and auric chloride to the crystallizing point. This double salt, which has the advantage of being non-deliquescent and neutral, may be regarded as sodium chloro-aurate, *i.e.* the sodium salt of chloro-auric acid, $HAuCl_4$, the compound which exists in a hydrochloric acid solution of auric chloride, and which can be obtained therefrom by evaporation in yellow crystals having the formula $HAuCl_4 4H_2O$.

With respect to the chemistry of the toning process, it appears to me that a great deal of unnecessary mystification has been introduced into some of the treatises on photography. Consider the state of affairs in the toning-bath. A film, composed of the reduction products of silver chloride and silver albumenate together with unaltered silver chloride and albumenate, is immersed in a solution of auric chloride. It is essential for good results that the toning-bath should be neutral, and the gold salt is accordingly

mixed with such substances as chalk, borax, sodium carbonate, phosphate, or acetate. Now it is well known that gold salts are most readily reducible—almost any reducing agent, organic or inorganic, will precipitate gold from a solution of the chloride. Thus, the action of sulphurous acid or ferrous sulphate may be taken as typical [J]:—

$$2AuCl_3 + 3H_2SO_3 + 3H_2O = Au_2 + 3H_2SO_4 + 6HCl$$
$$2AuCl_3 + 6FeSO_4 = Au_2 + Fe_2Cl_6 + 2Fe_2(SO_4)_3.$$

The toning solution may therefore be looked upon as containing a potential deposit of metallic gold ready to be precipitated on any reducing surface that may be bathed by it—just in the same way that the acid developing solution may be regarded as containing a potential deposit of metallic silver. The reduction products of the silver chloride and albumenate forming the positive image act as reducing agents,[1] and thus become

[1] If a reducing agent is put into the toning-bath, it reacts directly with the auric chloride, and prevents the precipitation of gold on the image. This is why it is so constantly urged in all practical manuals that no sodium thiosulphate should be allowed to get into the toning-bath.

covered with the deposit of gold which imparts the tone to the print. The unchanged silver chloride and albumenate cause no reduction, and therefore receive no deposit.

Much stress is laid by practical photographers upon the necessity for keeping the toning-bath neutral, and the reason for this appears to be that the presence of free acid checks the deposition of gold. Free hydrochloric acid would in fact play the part of a restrainer, and since this acid must necessarily result from the reduction of the auric chloride, it is requisite to have present some salt which at once enters into reaction with the acid and forms a soluble chloride with the liberation of an equivalent quantity of some milder acid, such as acetic, carbonic, &c. This is the function of the sodium acetate, carbonate, or other salt which is mixed with the toning solution. The sodium chloride thus formed no doubt in its turn helps to decompose the unaltered silver albumenate or any free silver nitrate present in the film, converting these compounds into silver chloride which is dissolved

out in the subsequent operation of fixing by thiosulphate.

The colour of finely-divided gold precipitated by reduction from a solution of one of its salts depends very much upon the state of concentration of the solution and the rate at which it is deposited. This is a very old observation due to Faraday. If the deposition takes place very slowly we get a red form of gold, if it takes place more rapidly the gold particles appear blue, these differences being doubtless due to different states of molecular aggregation. Now the reduction product of silver albumenate is naturally red, and it is therefore the blue form of gold which is required in order to give the print the desired tone. It is for this reason that the toning-bath is kept neutral; the deposition of gold must take place as rapidly as possible consistently with uniformity in order to insure the precipitation of the blue-particled form. The accumulation of a restrainer like hydrochloric acid in the toning-bath is therefore to be avoided; this is accomplished by the addition of the salts referred to, and by the

occasional neutralization of the bath solution with chalk.

After the print has been toned it is washed and fixed by immersion in a solution of sodium thiosulphate. The chemistry of this operation has already been sufficiently explained; but it is important to remember that in the silver print at this stage we have an image composed of the reduction products of silver albumenate and chloride coated with a deposit of gold, the remaining portions of the surface consisting chiefly of silver chloride formed by the action of the soluble chlorides in the toning-bath on the unaltered silver albumenate and the free silver nitrate which may have been retained by the film. The thiosulphate of course dissolves out all this silver chloride, but it is without action on the reduction product of the albumenate, so that the image is not affected by the fixing solution so far as concerns this organic silver constituent. But the reduction product of silver chloride is known to be decomposed by sodium thiosulphate,

leaving a residue of metallic silver (p. 45). The inorganic silver constituent (photochloride) of the image must therefore be decomposed in the fixing bath, and the finished print must be looked upon as consisting of an organic silver compound coated with silver and gold.[1] The importance of thoroughly washing out every trace of thiosulphate after fixing in order to insure the permanency of the print is well known to all photographers. One of the chief causes of the instability of silver prints is the imperfect removal of the soluble thiosulphate or the formation of the insoluble thiosulphate $AgNa(S_2O_3)$, owing to an insufficiency of sodium thiosulphate or to irregularity of action in the fixing-bath. In order to insure the complete destruction of the last trace of thiosulphate it is therefore recommended after the final washing of the print to immerse the latter in a weak solution of iodine in potassium iodide, the iodine

[1] Much of the reduction product of the silver chloride is no doubt re-chlorinated by auric chloride during the toning process, so that the proportion of metallic silver left in the finished print must be extremely small.

converting the thiosulphate into tetrathionate according to the well known reaction :—

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

The substitution of some other printing surface for the albumenized silver is a problem which has been solved in several ways. We may use for this purpose ferric or uranic salts, and develop by appropriate means in accordance with the chemical principles which have been sufficiently discussed in former lectures. One of the most promising of these recent methods gives an image composed of finely-divided platinum, and the chemistry of this platinotype process can be made readily intelligible by the aid of previous considerations. The fact that the salts of platinum are susceptible of photo-decomposition has already been alluded to (p. 20). This property was made known in 1832 by Herschel, and the photo-chemistry of the platinum compounds has been since investigated by Hunt, Gehlen, and many others. Time will not permit me to relate the various steps in the history of the process, and I need only add that it

has been brought to its present state of perfection chiefly by Mr. Willis, and that it has been thoroughly investigated by Pizzighelli and Hübl.

The first point to which attention must be directed is that the platinotype process is not a method of direct printing. Although the platinum salts, especially when in the platinous condition, are capable of being reduced to the metallic state by the action of light in the presence of organic reducing agents, this property has not yet been made available for the direct production of a platinum print. This is one of the problems awaiting future solution. The modern platinotype process depends upon the *indirect reduction* of the platinum salt by some compound which first undergoes photo-reduction, and is then made to react with the platinum salt. The principle concerned is somewhat similar to that which is made use of when a negative is intensified by platinic chloride (p. 338). In this case the metallic silver of the image is the reducing agent, and if we suppose the platinum solution to act for a sufficient time, the whole of the silver would be converted into

chloride, and the image replaced by its equivalent in metallic platinum. On fixing with thiosulphate the silver chloride would be dissolved away, and the platinum image left. This illustrates the indirect production of a platinotype print [K].

In the modern process the photo-reducible compound is a ferric salt, viz., ferric oxalate, the mode of decomposition of which is familiar to you (p. 16). The platinum is supplied by the reduction of a platinous compound, potassium chloroplatinite, concerning which it is desirable to give a little further information. Platinum tetrachloride, $PtCl_4$, can by cautious heating to 300° C. be made to give off two atoms of chlorine, leaving platinous chloride, $PtCl_2$. This last salt is insoluble in water, but is soluble in hydrochloric acid, and the solution contains chloroplatinous acid, H_2PtCl_4. Just in the same way the hydrochloric acid solution of platinic chloride is regarded as containing chloroplatinic acid, H_2PtCl_6. Now on mixing a solution of chloroplatinous acid with potassium chloride and crystallizing, we get potassium chloroplatinite, K_2PtCl_4. In practice this salt is con-

veniently prepared by reducing the chloroplatinate with moist, freshly-prepared cuprous chloride:—

$$K_2PtCl_6 + Cu_2Cl_2 = K_2PtCl_4 + 2CuCl_2.$$

On filtering and evaporating the solution the crystals of the chloroplatinite separate out.

In order to prepare paper for platinotype printing, it is first sized so as to prevent the sensitizing solutions from being absorbed, and is then coated with a solution containing ferric oxalate and potassium chloroplatinite, made slightly acid with oxalic acid. The sensitized paper is thoroughly dried, and is then exposed under a negative in the usual way. The effect of this exposure is to produce an image in ferrous oxalate by photochemical reduction, this image being imbedded in a film of potassium chloroplatinite, because the latter salt does not undergo any appreciable amount of decomposition during the short exposure that is necessary to decompose the ferric salt. Up to this point the platinum salt has taken no part in the process. Now ferrous oxalate is insoluble in water but is soluble in potassium oxalate, so that

on immersing the print in a solution of this salt (generally used warm) the ferrous oxalate is dissolved out, and at the moment of its solution reacts with the chloroplatinite, reducing the latter to the metallic state:—

$$3K_2PtCl_4 + 6FeC_2O_4 = 3Pt + 2Fe_2(C_2O_4)_3 + Fe_2Cl_6 + 6KCl$$

The amount of ferrous oxalate produced on any part of the ferric-coated surface is, broadly speaking, proportional to the amount of light which reaches that part of the surface. The high lights of the object, corresponding to the densest parts of the negative, thus correspond with the smallest amount of ferrous oxalate, and the deepest shadows of the object similarly give rise to the formation of the largest amount of ferrous salt, while the half-tones produce an intermediate quantity of ferrous oxalate. In this manner the image is impressed in ferrous salt, and the latter, when the print is immersed in the potassium oxalate bath, reduces the chloroplatinite to a proportional extent, so that the ferrous image is replaced by its platinum

equivalent. The potassium oxalate solution thus causes the image to be developed, and at the same time partially fixes it by removing most of the unaltered ferric salts. The latter are finally dissolved out by repeatedly washing the print with dilute hydrochloric acid. It is hardly necessary to add that an image composed of finely-divided platinum is practically indestructible by all those agents which are capable of affecting a silver print.

A number of printing processes, and especially the photo-mechanical methods, are based on the action of light upon a film of chromatized gelatine (p. 23). The change of colour undergone by a solution of potassium or ammonium dichromate when spread over a surface of paper and exposed to light was made use of in a printing process devised by Mungo Ponton in 1839. The property possessed by a mixture of potassium dichromate and gelatine of becoming insoluble in water under the influence of light was first utilized in a printing process described in 1852 by Fox Talbot, and the conversion of such a film into a coloured print by

mixing the gelatine with a pigment was effected in 1855 by Poitevin. The nature of the chemical change undergone by the chromatized gelatine was first suggested by Swan in 1870, and nearly all that has since been made known concerning the photo-chemical action of chromium compounds upon organic colloidal substances is due to the investigations of Eder published in 1878.[1] A discussion of the various processes depending upon the use of chromatized gelatine would take us too far from the domain of chemistry on the present occasion. One of the best known is that made use of by the Autotype Company, specimens of whose work have been forwarded for your inspection. This process, as at present worked, is the outcome of a method of printing with pigmented gelatine which was first successfully applied by Swan in 1864, and a brief description will enable you to see how the action of light upon chromatized gelatine is practically utilized for the production of the coloured prints before you.

[1] *Ueber die Reactionen der Chromsäure und der Chromate auf Gelatin, Gummi, Zucker, &c.* Wien, 1878.

In the autotype process the colouring matter and gelatine are first made into a homogeneous mixture, and the latter, after being sensitized with potassium dichromate, is spread as a uniform film over the surface of paper. The sensitive film when dry is placed under the negative which is to be printed from and exposed to light in the usual way. The image at this stage is invisible because the insoluble portions of the film do not differ in appearance from those portions which are unacted upon by light. Now the extent to which the chromatized gelatine is rendered insoluble is dependent upon the amount of light which reaches any part of the sensitive surface. The high lights of the object, corresponding to the darkest parts of the negative, therefore give the smallest quantity of insoluble gelatine, the shadows of the object give the largest quantity, and the half-tones an intermediate quantity of insoluble gelatine. But the whole surface of the film in contact with the negative is obviously rendered more or less insoluble, so that *development must take place from the back of the film.* When the printing operation

is over, the latter is therefore transferred to a paper support which holds it during development, the surface which was in contact with the negative being held by the support, and the film being thus stripped off the paper to which it was originally attached. On treatment with hot water the film is now attacked from behind and development takes place—that is to say the various portions of the gelatine are dissolved away according to their solubility. Where the light has penetrated most, there most of the gelatine will be left: where the least light has been transmitted by the negative, the smallest quantity of gelatine will be left, and so forth. At this stage the developed print is consequently an image in relief on the surface of a gelatine film. The developed print on being again transferred to a white surface thus gives a coloured picture in which the depths of colour are proportional to the depth of pigmented gelatine through which the white light has to pass [L]. The high lights of the object correspond to the thinnest layers, the shadows to the thickest layers, and the half-tones to layers of coloured

gelatine of intermediate thickness. In this way the print is formed, its colour being of course determined by the pigment mixed with the gelatine. This explanation will suffice to make intelligible the principle of the mode of working. It is perhaps necessary to add that the image is laterally reversed by the processes of transference, but this can be obviated by the use of an intermediate temporary support. The introduction of this modification is due to Mr. J. R. Sawyer, through whose kindness you will have an opportunity of seeing how the whole autotype process is practically carried out.[1]

[1] At the conclusion of the lecture a demonstration of the process was given by a representative of the Autotype Company.

APPENDIX TO LECTURE IX.

A (p. 332).—A glass plate is coated with a film of collodion salted with strontium chloride, and is then sensitized (in red light) in a silver nitrate bath. One half of the plate (wet with the bath solution) is then immersed in a strong solution of sodium thiosulphate, and the other half in a very weak solution of the same salt. The first half of the plate becomes quite clear, and the second half receives a coating of the dark insoluble double salt.

B (p. 334).—A design in metallic silver is produced, as in Experiment H, p. 180. The paper is washed, immersed in a sodium thiosulphate bath, and then again washed with water. On brushing over the design with a solution of mercuric chloride it gradually disappears. The paper is then washed in water and torn into five or six strips for subsequent experiments.

C (p. 334).—A portion of the paper used in the last experiment is brushed over with dilute am-

monia, when the design again comes out dark on a white ground.

D (p. 335).—Another portion of the paper from Experiment B is brushed over with a solution of ammonium sulphide, and another strip with sodium sulphite.

E (p. 335).—A solution of potassio-ferrous oxalate is prepared by adding a cold saturated solution of ferrous sulphate to about 3—4 times its volume of a cold saturated solution of potassium oxalate. Another strip of the paper from Experiment B is then brushed over with this solution, when, as before, the design comes out dark.

F (p. 336).—A solution of potassium cyanide is run into a solution of silver nitrate until the precipitate first formed is just dissolved. Another strip from Experiment B is then brushed over with this solution; the design comes out dark.

G (p. 340).—A silver design is produced as in Experiment B, and the paper is then torn into two strips, one of which is floated on a solution of cupric chloride and the other on a solution of ferric chloride. In both cases the design gradually bleaches.

H (p. 343).—A solution of silver nitrate is added to a solution of albumen in water in order to show the formation of a curdy precipitate.

I (p. 351).—Paper is coated with silver tartrate by floating it on solutions of potassium tartrate

and silver nitrate alternately. The experiment is performed as described in the text.

J (p. 354).—A design is painted on a sheet of paper with a strong solution of ammonio-ferrous sulphate thickened with starch paste. When the design is nearly dry the paper is floated, face downwards, on an ordinary gold toning-bath solution till the marking comes out of a brownish colour. The experiment succeeds better if the gold solution is warmed before using.

K (p. 361).—A design in silver is produced on paper, as in Experiment B. The paper is torn in half, and one portion floated, face downwards, for some minutes on a solution of platinic chloride. Both halves are then passed through a dilute nitric acid bath, when the unplatinized portion of the design is completely dissolved away, while the platinized portion is not attacked, showing that the silver of the design has, in the latter case, been replaced by platinum.

L (p. 367).—The increase in the depth of shade by increasing the thickness of the coloured film can be easily shown by placing a thin sheet of coloured gelatine in the path of the electric beam, and then folding it so as to get double and quadruple thicknesses.

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